

## General Anharmonic Force Constants of Carbon Dioxide

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Twelve force constants in the general quartic force field of carbon dioxide have been determined by the least squares method from spectroscopic data on  $C^{12}O_2^{16}$  and  $C^{13}O_2^{16}$  together with the four third-order parameters, i.e.,  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ , and  $\delta$  which appear in the Fermi coupling off-diagonal elements. It is shown that inclusion of these third-order parameters is indispensable to obtain a reasonable set of anharmonic force constants. From these force constants, consistent sets of vibrational constants ( $\omega_s$ ,  $x_{ss'}$ ), Fermi coupling constants ( $W_c$ ), and rotation-vibration coupling constants ( $\alpha_s$ ) have been derived for  $C^{12}O_2^{16}$ ,  $C^{13}O_2^{16}$ ,  $C^{12}O^{16}O^{18}$  and  $C^{13}O^{16}O^{18}$ . The calculated vibrational energy levels and rotational constants agree well with those obtained experimentally. A potential energy contour map of carbon dioxide is also given and discussed.

### INTRODUCTION

In a previous paper (1) we described a method for the least squares determination of anharmonic force constants from spectroscopic data. This method was applied to the carbon dioxide and hydrogen cyanide molecules (1, 2). As is well known, the vibrational energy levels of polyatomic molecules are expressed, to the second order of approximation, by the formula (3),<sup>1</sup>

$$E/hc = E_0/hc + \sum_s \omega_s(v_s + d_s/2) + \sum_{s \geq s'} x_{ss'}(v_s + d_s/2)(v_{s'} + d_{s'}/2) + \sum_{t \geq t'} x_{t_t t_t} l_t l_{t'} \quad (1)$$

and the rotational constant associated with each vibrational level by

$$B_v^\xi = B_e^\xi - \sum_s \alpha_s^\xi(v_s + d_s/2) \quad (2)$$

where  $\xi$  is  $x$ ,  $y$ , or  $z$ .

In Refs. (1) and (2), we used two alternative procedures for selecting the spectroscopic data. In the first method (Method I), we applied a least squares technique to obtain the anharmonic force constants<sup>2</sup> which give the best fit to

<sup>1</sup> We follow the notations given in Ref. (3), unless otherwise stated. As stated in this reference, Eqs. (1) and (2) apply to a resonance-free case.

<sup>2</sup> In the present paper, "anharmonic force constants" refer to the coefficients appearing in Eq. (4) in which the molecular potential is expressed in terms of curvilinear internal

the derived constants of  $\omega_s$ ,  $x_{ss'}$ , and  $\alpha_s$ , whereas the adjustment was made in the second method (Method II) to the band origins of the observed fundamentals, overtones and combination tones, and the differences in observed rotational constants ( $B_v - B_0$ ). As discussed in Refs. (1) and (2), we preferred Method II over Method I, since in Method I we must either ignore the correlations between the derived constants of  $\omega_s$ ,  $x_{ss'}$ , and  $\alpha_s$ , or employ the more cumbersome general least squares method in which the weight matrix is no longer diagonal (2). In the case of carbon dioxide, however, the normal equations were not stable for Method II, and we could not obtain a reasonable set of force constants unless some constants were constrained at fixed values.

A number of investigations, both theoretical and experimental, have recently been carried out on the carbon dioxide molecule (4-7). Amat and Pimbert (4) have pointed out that the traditional method for deriving vibrational constants and Fermi coupling constant  $W_s$ , if applied to the case of strong Fermi resonance, would lead to isotopically inconsistent results. They have also shown that the vibrational constants of  $C^{12}O_2^{16}$  and other isotopic species given by Courtoy (8, 9), for example, predict the vibrational energy levels for each isotopic species very precisely, but lead to an imaginary value of  $k_{122}$ , when the following relationship

$$x_{22} + 3x_{t_2t_2} = (-1/2)k_{122}^2[(1/\omega_1) - 1/2(2\omega_2 + \omega_1)] \quad (3)$$

is applied. Amat and Pimbert have also given a more refined method for analyzing the vibrational and rotational constants when Fermi resonance is considered.

More recently, Gordon and McCubbin have made precise infrared measurements on the bands of  $C^{12}O_2^{16}$  molecule in the 16  $\mu$  and 2.8  $\mu$  regions (5, 6). They derived, by using the method of Amat and Pimbert, a new set of vibrational constants,  $\omega_s$ ,  $x_{ss'}$ , and  $x_{t_2t_2}$  for  $C^{12}O_2^{16}$  which differs significantly from that given by Courtoy (8, 9).

The above facts indicate that, in determining anharmonic force constants from spectroscopic data, utmost care must be taken in the treatment of Fermi resonance. Therefore, it was considered worthwhile to recalculate the force constants in the general quartic force field for carbon dioxide, applying various kinds of constraints for the Fermi coupling off-diagonal elements. We have used exclusively Method II, in which the force constants were adjusted to fit the band origins and rotational constants of the vibration-rotation bands of  $C^{12}O_2^{16}$  and  $C^{13}O_2^{16}$ . The main objective of the present investigation is twofold: one is to obtain a more refined set of constants of the general quartic force field

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coordinates (1); they include the quadratic force constants,  $K_{ij}$ , as well as the cubic and quartic force constants,  $K_{ijk}$  and  $K_{ijkl}$ . "Vibrational constants" are the ones appearing in Eq. (1), namely  $\omega_s$  and  $x_{ss'}$ , by which the vibrational energy levels are described, whereas "rotation-vibration coupling constants" are the quantities  $\alpha_s$  appearing in Eq. (2) by which the unperturbed rotational constant of each vibrational level may be expressed.

for carbon dioxide in order to provide a deeper understanding of the intramolecular potential in polyatomic molecules. One may also regard the above procedure as reducing a large number of complicated spectroscopic data on carbon dioxide to 12 basic force constants which are invariant to isotopic substitutions. The other objective is, therefore, to obtain a more consistent set of vibrational constants, rotation—vibration coupling constants, and Fermi coupling constants for various isotopic species of carbon dioxide from those force constants. The conventional approach to the problem of obtaining the vibrational constants is limited to one isotopic species: the  $\omega$ 's,  $x$ 's, and  $\alpha$ 's are obtained separately for each isotopic species. The various isotopic relationships between the  $\omega$ 's,  $x$ 's and  $\alpha$ 's are not necessarily fulfilled by this approach.<sup>3</sup> After values of the 12 anharmonic force constants of carbon dioxide have been determined, we may compute for any isotopic species, sets of the vibrational and vibration—rotation coupling constants,  $\omega$ 's,  $x$ 's, and  $\alpha$ 's, which fully satisfy the isotopic relationships. With the above objectives in mind, we have re-evaluated the anharmonic force constants of the carbon dioxide molecule. The results are given and discussed in this paper.

#### DETERMINATION OF ANHARMONIC FORCE CONSTANTS

Since a general procedure for the determination of anharmonic force constants was given in detail in Ref. (1), only a brief outline of the calculation is given in this section. The molecular potential is expressed as a function of the curvilinear internal coordinates through quartic terms, and it is of the following form for the case of a linear symmetrical triatomic molecule:

$$\begin{aligned}
 V = & K_{11}(R_1^2 + R_3^2) + K_{13}R_1R_3 + K_{22}R_2^2 + K_{111}(R_1^3 + R_3^3) \\
 & + K_{122}(R_1 + R_3)R_2^2 + K_{133}(R_1 + R_3)R_1R_3 + K_{1111}(R_1^4 + R_3^4) \\
 & + K_{1113}(R_1^2 + R_3^2)R_1R_3 + K_{1133}R_1^2R_3^2 + K_{1122}(R_1^2 + R_3^2)R_2^2 \\
 & + K_{1223}R_1R_2^2R_3 + K_{2222}R_2^4,
 \end{aligned} \tag{4}$$

where  $R_1$  and  $R_3$  are the two stretching coordinates, while  $R_2$  is the bending coordinate. Starting from assumed values for the 12 force constants in Eq. (4), two successive transformations of the coordinate systems are carried out. The first is a nonlinear transformation from curvilinear internal to difference Cartesian coordinates,<sup>4</sup> and the second is a linear transformation from difference

<sup>3</sup> For such a simple molecule as carbon dioxide, it is not impossible to determine a consistent set of the vibrational constants by applying the least-squares technique to the known data of entire isotopic species with the proper constraints in the values of vibrational constants; for example  $\omega_1(\text{C}^{13}\text{O}_2^{16}) = \omega_1(\text{C}^{13}\text{O}_2^{16})$ ,  $x_{11}(\text{C}^{12}\text{O}_2^{16}) = x_{11}(\text{C}^{18}\text{O}_2^{16})$  and so on. This is, however, extremely cumbersome and the isotopic relationships for some  $x_{ss'}$  and for some  $\alpha_s$  are not trivial. Therefore, we prefer to reduce the observed data to 12 GVFF constants.

<sup>4</sup> As indicated in Eqs. (4–6) in Ref. (1), the first transformation coefficients depend only upon the structural parameters of a given molecule.

Cartesian to dimensionless normal coordinates ( $q_i$ 's), by which the molecular potential is expressed as,

$$V = \sum_i (\frac{1}{2})\omega_i q_i^2 + \sum_{i \geq j \geq k} k_{ijk} q_i q_j q_k + \sum_{i \geq j \geq k \geq l} k_{ijkl} q_i q_j q_k q_l, \quad (5)$$

where  $\omega_i$  is the harmonic frequency, and  $k_{ijk}$  and  $k_{ijkl}$  are, respectively, the cubic and quartic force constants in dimensionless normal coordinates.

The vibrational and rotational constants in Eqs. (1) and (2) are evaluated from  $\omega_i$ ,  $k_{ijk}$ ,  $k_{ijkl}$ , using Nielsen's formulae (3). Finally, each vibrational energy level and its rotational constant are calculated and compared with the observed. As described in Ref. (1), the above procedure should be modified when some energy levels are involved in resonance. In this case, the first-order corrections to the vibrational energy levels are obtained by solving a secular determinant which has nonvanishing off-diagonal elements, and some expressions for  $x_{ss'}$  which have diminishing denominators must be changed. The treatment of Fermi-Dennison resonance in the specific case of carbon dioxide is described in the following section.

In order to find the least squares corrections to the initial anharmonic force constants, a finite difference method is employed (10). In this method, the Jacobian matrix elements are obtained by changing the value of each force constant in turn by a small amount. Then, the correction vector  $\Delta\mathbf{K}$  to the initial force constants is found by solving the well-known simultaneous equations:

$$(\tilde{\mathbf{J}}\mathbf{P}\mathbf{J})\Delta\mathbf{K} = \tilde{\mathbf{J}}\mathbf{P}\Delta\mathbf{v}, \quad (6)$$

where  $\mathbf{P}$  is a diagonal weight matrix,  $\Delta\mathbf{v}$  represents a column vector consisting of the differences between the observed and calculated values of the corresponding data. This process is repeated until corrections to the force constants become negligibly small.

The vibrational energy levels and rotational constants used in the present investigation are taken from the recent high-resolution measurements of Gordon and McCubbin (5, 6) and those of Courtoy (8, 9). Reference is also made to the publications of Plyler, Blaine, and Tidwell (11) and Taylor, Benedict, and Strong (12). The vibrational levels and rotational constants of  $\text{C}^{13}\text{O}_2^{16}$  are mainly taken from Courtoy (9). The observed data: 33 vibrational levels and 31 rotational constants for  $\text{C}^{12}\text{O}_2^{16}$  and 26 vibrational levels and 22 rotational constants for  $\text{C}^{13}\text{O}_2^{16}$ , are given in the first column of Table I, along with the corresponding weights in the second column. As discussed in Ref. (1), the levels associated with higher vibrational quantum numbers are weighted less, since we have dropped the higher terms such as

$$\sum_{s \geq s' \geq s''} y_{ss's''} (v_s + d_s/2)(v_{s'} + d_{s'}/2)(v_{s''} + d_{s''}/2),$$

from Eq. (2).

Numerical computations were carried out with a Hitac 5020E computer in the

Table I. The Observed and Calculated Vibrational Levels (cm<sup>-1</sup>) and Rotational Constants (10<sup>-4</sup> cm<sup>-1</sup>) for C<sup>12</sup>O<sub>2</sub> and C<sup>13</sup>O<sub>2</sub>.<sup>a</sup>

Level	ν <sub>obs</sub>	(Obs. - Calc.) X 100												
		wt.	(i)	(ii)	(iii)	(iv)	(v)	(B <sub>v</sub> -B <sub>0</sub> )	wt.	(i)	(ii)	(iii)	(iv)	(v)
$\left[ \begin{array}{l} 1 \ 0 \ 0 \\ 0 \ 2 \ 0 \end{array} \right]$	1388.19	1.0	219	89	45	18	16	-0.09	1.0	101	125	79	20	8
	1285.41	1.0	181	29	13	19	19	2.66	1.0	157	163	101	6	7
$\left[ \begin{array}{l} 1 \ 1 \ 0 \\ 0 \ 3 \ 0 \end{array} \right]$	1285.41	1.0	237	74	39	21	20	6.44	1.0	110	191	108	61	54
	1932.47	1.0	231	82	35	34	33	9.56	1.0	155	96	2	60	63
$\left[ \begin{array}{l} 1 \ 0 \ 1 \\ 0 \ 2 \ 1 \end{array} \right]$	3714.78	1.0	158	104	16	16	12	-31.55	1.0	136	115	61	10	13
	3612.84	1.0	131	104	32	3	5	-27.15	1.0	116	112	62	21	17
$\left[ \begin{array}{l} 1 \ 1 \ 1 \\ 0 \ 3 \ 1 \end{array} \right]$	4390.63	1.0	153	142	35	8	5	-24.20	1.0	88	130	39	19	12
	4247.71	1.0	139	125	1	31	26	-19.76	1.0	189	127	41	24	16
$\left[ \begin{array}{l} 2 \ 0 \ 1 \\ 1 \ 2 \ 1 \\ 0 \ 4 \ 1 \end{array} \right]$	5099.61	1.0	166	202	42	19	3	-27.03	1.0	177	197	36	13	1
	4977.81	1.0	68	59	73	2	11	-36.69	1.0	5	62	40	46	30
$\left[ \begin{array}{l} 1 \ 2 \ 1 \\ 0 \ 4 \ 1 \end{array} \right]$	4853.63	1.0	201	246	47	5	7	-20.31	1.0	251	202	45	25	14
	5061.78	0.1	275	338	318	76	29	-16.92	0.1	38	142	23	25	10
$\left[ \begin{array}{l} 3 \ 0 \ 1 \\ 2 \ 2 \ 1 \\ 1 \ 4 \ 1 \\ 0 \ 6 \ 1 \end{array} \right]$	4888.00	0.1	42	31	302	92	55	-12.80	0.1	209	88	25	27	36
	6503.05	0.1	64	380	52	20	7	-22.30	0.1	252	320	10	58	18
$\left[ \begin{array}{l} 2 \ 2 \ 1 \\ 1 \ 4 \ 1 \\ 0 \ 6 \ 1 \end{array} \right]$	6347.81	0.1	51	140	19	45	44	-37.65	0.1	154	97	36	38	55
	6227.88	0.1	22	83	67	27	12	-35.25	0.1	82	142	19	32	8
$\left[ \begin{array}{l} 6 \ 0 \ 1 \end{array} \right]$	6075.93	0.1	65	374	42	24	41	-15.30	0.1	169	77	226	184	207

Table I. (Continued)

	$\nu_{\text{obs}}$	wt.	(i)	(ii)	(iii)	(iv)	(v)	$(B_v - B_0)$	wt.	(i)	(ii)	(iii)	(iv)	(v)
$\begin{bmatrix} 3 & 1^1 & 1 \\ 2 & 3^1 & 1 \\ 1 & 5^1 & 1 \\ 0 & 7^1 & 1 \end{bmatrix}$	7204.22	0.1	46	589	112	31	21	-18.55	0.1	269	371	12	80	23
	7024.03	0.1	81	262	168	59	47	-27.80	0.1	95	122	29	57	63
	6893.91	0.1	96	27	236	35	14	-25.70	0.1	66	37	115	84	115
	6688.54	0.1	210	308	277	58	97	-8.50	0.1	431	303	72	7	24
$\begin{bmatrix} 1 & 0 & 3 \\ 0 & 2^0 & 3 \end{bmatrix}$	8294.01	0.1	8	97	98	59	48	-94.10	0.1	175	53	9	17	16
	8192.62	0.1	36	193	33	33	32	-86.90	0.1	28	7	24	38	24
	667.38	1.0	61	77	82	13	15	7.30	1.0	53	7	7	10	7
	1335.13	1.0	37	14	103	67	38	14.47	1.0	93	28	26	33	27
$\begin{bmatrix} 0 & 3^0 & 0 \\ 0 & 0 & 1 \\ 0 & 1^1 & 2 \\ 0 & 0 & 3 \end{bmatrix}$	2003.28	0.01	295	274	558	159	60	21.50	0.1	119	63	60	70	61
	2349.16	1.0	23	11	22	1	0	-30.90	1.0	64	47	37	30	32
	5316.09	0.1	25	60	64	20	9	-53.70	0.1	5	21	0	10	10
	6972.49	0.1	6	0	11	23	21	-92.25	0.1	148	95	65	45	50
$\begin{bmatrix} 0 & 0 & 5 \\ 0 & 1^1 & 3 \\ 0 & 5^0 & 0 \\ 0 & 2^2 & 2 \end{bmatrix}$	11496.85	0.1	33	1	16	12	8	-153.50	0.1	222	133	83	50	58
	7602.85	0.1	27	101	99	44	27	-84.50	0.1	50	57	27	10	12
	3341.80	0.0	1397	1407	2379	385	28							
	5960.08	0.1	269	361	454	12	66							

Table I. (Continued.)

Level	$\nu_{\text{obs}}$	(Obs. - Calc.) X 100		(Obs. - Calc.) X 100										
		wt.	(i)	(ii)	(iii)	(iv)	(v)	(B <sub>v</sub> -B <sub>0</sub> )	wt.	(i)	(ii)	(iii)	(iv)	(v)
[ <sup>1</sup> 0 1] [ <sup>0</sup> 2 <sup>0</sup> 1]	3632.92	1.0	<u>26</u>	<u>73</u>	<u>25</u>	0	<u>5</u>	-35.24	1.0	<u>165</u>	<u>110</u>	<u>58</u>	4	<u>11</u>
	3527.71	1.0	13	33	<u>45</u>	3	<u>3</u>	-22.25	1.0	119	82	34	<u>18</u>	<u>10</u>
[ <sup>1</sup> 1 <sup>1</sup> 1] [ <sup>0</sup> 3 <sup>1</sup> 1]	4288.09	1.0	<u>138</u>	<u>142</u>	<u>43</u>	6	0	-26.70	1.0	<u>69</u>	<u>81</u>	9	49	39
	4147.63	1.0	143	145	31	20	21	-16.10	1.0	211	125	40	3	13
[ <sup>2</sup> 0 1] [ <sup>1</sup> 2 <sup>0</sup> 1] [ <sup>0</sup> 4 <sup>0</sup> 1]	4991.31	1.0	<u>354</u>	<u>310</u>	<u>91</u>	<u>16</u>	<u>14</u>	-35.35	1.0	<u>273</u>	<u>218</u>	<u>66</u>	21	<u>7</u>
	4887.35	1.0	<u>11</u>	<u>7</u>	<u>31</u>	<u>2</u>	<u>5</u>	-33.95	1.0	19	69	66	25	28
	4748.01	1.0	243	178	<u>111</u>	10	<u>13</u>	-13.95	1.0	292	192	24	<u>13</u>	2
[ <sup>1</sup> 2 <sup>2</sup> 1] [ <sup>0</sup> 4 <sup>2</sup> 1]	4940.49	0.1	13	58	317	62	92	-18.90	0.1	18	<u>57</u>	62	83	77
	4772.64	0.1	497	469	395	71	108	-9.60	0.1	275	134	20	<u>5</u>	7
[ <sup>2</sup> 1 <sup>1</sup> 1] [ <sup>1</sup> 3 <sup>1</sup> 1] [ <sup>0</sup> 5 <sup>1</sup> 1]	5662.64	0.1	<u>542</u>	<u>377</u>	21	4	18	-28.20	0.1	<u>213</u>	<u>216</u>	0	41	19
	5520.32	0.1	<u>2</u>	19	7	<u>1</u>	3	-25.95	0.1	<u>27</u>	<u>53</u>	<u>55</u>	<u>82</u>	<u>77</u>
	5357.39	0.1	536	370	<u>30</u>	29	5	-8.50	0.1	416	276	45	30	42
[ <sup>3</sup> 0 1] [ <sup>2</sup> 2 <sup>0</sup> 1] [ <sup>1</sup> 4 <sup>0</sup> 1] [ <sup>0</sup> 6 <sup>0</sup> 1]	6363.58	0.1	<u>946</u>	<u>617</u>	20	<u>19</u>	14	-32.00	0.1	<u>350</u>	<u>319</u>	<u>14</u>	31	<u>5</u>
	6241.93	0.1	<u>284</u>	<u>170</u>	<u>31</u>	<u>47</u>	<u>12</u>	-43.80	0.1	<u>246</u>	<u>130</u>	<u>48</u>	<u>74</u>	<u>81</u>
	6119.56	0.1	104	53	<u>190</u>	<u>29</u>	<u>52</u>	-26.45	0.1	199	189	79	46	56
	5951.53	0.1	772	423	<u>263</u>	12	<u>58</u>	-5.80	0.1	487	327	<u>8</u>	11	20

Table I. (Continued.)

Level	$\nu_{\text{obs}}$	wt.	(i)	(ii)	(iii)	(iv)	(v)	( $B_v - B_0$ )	wt.	(i)	(ii)	(iii)	(iv)	(v)
$\begin{bmatrix} 1 & 0 & 3 \\ 0 & 2 & 0 \\ & & 3 \end{bmatrix}$	8089.01	0.1	<u>177</u>	<u>151</u>	<u>119</u>	75	54	-94.90	0.1	<u>202</u>	<u>56</u>	13	13	0
	7981.77	0.1	112	8	<u>70</u>	6	8	-79.60	0.1	114	56	29	65	65
$0 \ 1^1 \ 0$	648.91	1.0	<u>31</u>	<u>47</u>	<u>57</u>	28	23	7.00	1.0	60	1	2	<u>1</u>	2
$0 \ 0 \ 1$	2283.48	1.0	20	8	18	<u>3</u>	<u>2</u>	-29.80	1.0	<u>65</u>	<u>48</u>	<u>38</u>	<u>32</u>	<u>33</u>
$0 \ 0 \ 3$	6780.14	0.1	14	3	15	<u>17</u>	<u>14</u>	-88.70	0.1	<u>126</u>	<u>74</u>	<u>45</u>	<u>25</u>	<u>30</u>
$0 \ 1^1 \ 3$	7393.96	0.1	20	84	77	<u>37</u>	<u>23</u>	-81.20	0.1	<u>16</u>	<u>23</u>	7	23	22
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ & & 0 \end{bmatrix}$	1370.05	1.0	42	49	3	<u>18</u>	<u>16</u>							
	1265.81	1.0	<u>44</u>	71	<u>16</u>	6	<u>3</u>							
$\begin{bmatrix} 1 & 1^1 & 0 \\ 0 & 3^1 & 0 \end{bmatrix}$	2037.50	1.0	<u>50</u>	<u>177</u>	<u>73</u>	23	17							
	1896.93	1.0	51	167	40	29	23							

Footnote to Table I.

The values given in Columns (i)-(v) are computed from the corresponding sets of force constants given in Table II. Only the differences between observed and calculated frequencies (in a hundredth  $\text{cm}^{-1}$ ) and rotational constants (in  $10^{-6} \text{cm}^{-1}$ ) are given. Negative differences are underlined.



Computation Centre of the University of Tokyo. The programs for the anharmonic problems have been written in Fortran IV along the lines indicated in Ref. (1), although several modifications have been made. The modifications are, however, rather technical in nature to shorten the computation time, and they do not alter the general principle given in Ref. (1). We adopted the value of  $r_e = 1.1600 \text{ \AA}$  for the equilibrium C-O bond distance.

#### FERMI RESONANCE IN CARBON DIOXIDE

The problem of Fermi resonance in carbon dioxide, for which the fundamental  $\nu_1^0$  is located very close to the overtone  $(2\nu_2)^0$  is well known. In order to obtain the vibrational energy levels involved in Fermi resonance, we have to solve a secular determinant for a given polyad. Nielsen (3) showed that the off-diagonal matrix elements of the determinant are expressed, to the first order of approximation as,

$$(v_1, v_2, \ell_2, v_3 | v_1 - 1, v_2 + 2, \ell_2, v_3) = (W_e/2)[(v_2 + 2)^2 - \ell_2^2]^{1/2} v_1^{1/2} \quad (7)$$

where  $W_e = -k_{122}/\sqrt{2}$ . In interpreting the spectrum of carbon dioxide, the parameter  $W_e$  in Eq. (7) was found to vary with the vibrational quantum numbers (12). Amat and Goldsmith (13), and Maes (14) have shown that  $W_e$  must be replaced by

$$W_r = W_e + \lambda_1 v_1 + \lambda_2 (v_2 + 2) + \lambda_3 (v_3 + 1/2), \quad (8)$$

if third-order correction terms are taken into account. Maes (14) has pointed out that the Fermi coupling term also varies with the rotational quantum number  $J$ , and a term  $\delta J(J + 1)$  should be added to Eq. (8). Therefore, the Fermi coupling off-diagonal element is expressed as

$$(1/2)[-k_{122}/\sqrt{2} + \lambda_1 v_1 + \lambda_2 (v_2 + 2) + \lambda_3 (v_3 + 1/2) + \delta J(J + 1)] \times [(v_2 + 2)^2 - \ell_2^2]^{1/2} v_1^{1/2}. \quad (9)$$

Usually, the perturbed (observed) rotational constants ( $B_i$ ) of a given polyad are related to the unperturbed constants ( $B_j^0$ ) by the following relation:

$$B_i = \sum_j B_j^0 L_{ji}^2, \quad (10)$$

where  $L_{ji}$  represents a fractional contribution of the  $j$ th unperturbed level to the  $i$ th perturbed level. This relationship must be modified in the present approximation, since the constant  $\delta$  appearing in the nonvanishing off-diagonal elements also contributes to the  $B_i$ 's:

$$B_i = \sum_j L_{ji} L_{ki} R_{jk}^0, \quad (11)$$

where  $R_{ij}^0 = B_i^0$ , and  $\delta$  comes into the off-diagonal element,  $R_{ij}^0$ , in the manner indicated in Eq. (9). Amat and Pimbert emphasized that when Fermi resonance is very strong, i.e., the energy difference between the unperturbed levels is small,

$\delta$  should be taken into consideration. They have shown that a very consistent rotational analysis can be made from the assumed value of  $2.0 \times 10^{-4} \text{ cm}^{-1}$  for  $\delta$ . Amat and Pimbert have also pointed out that there exist off-diagonal matrix elements of the form

$$(v_1, v_2, \ell_2, v_3 | v_1 - 2, v_2 + 4, \ell_2, v_3) \\ = u\{[(v_2 + 2)^2 - \ell_2^2][(v_2 + 4)^2 - \ell_2^2]v_1(v_1 - 1)\}^{1/2}, \quad (12)$$

which may contribute to the vibrational energy levels of triads, tetrads, and higher polyads.

In order to calculate the third-order terms in the Fermi coupling constant, which are very complicated functions of molecular geometry and vibration constants, we have to expand Eq. (4) further to include quintic and hexic terms in the internal coordinates.<sup>5</sup> This could be done in principle, but it seems quite impractical. For this reason we used Eq. (7) in our previous paper (1). However, the work of Amat and Pimbert has convinced us that the use of  $\lambda$ 's as well as  $\delta$  is indispensable, and their omission from the Fermi coupling off-diagonal elements may put too much strain on the values of the force constants and lead to unsatisfactory results. In the present calculation, we have included all or a part of the  $\lambda$ 's,  $u$  and  $\delta$  (hereafter referred to simply as "third-order parameters") in parametric forms, to obtain the perturbed frequencies and rotational constants involved in Fermi polyads. Therefore, the 12 anharmonic force constants of Eq. (4) as well as the third-order parameters are refined to obtain the best least squares agreements to 111 vibrational levels and rotational constants of  $\text{C}^{12}\text{O}_2^{16}$  and  $\text{C}^{13}\text{O}_2^{16}$ . The results are given in the following section.

#### RESULTS AND DISCUSSION

The converged sets of the anharmonic force constants adjusted with or without the third-order parameters are listed in Table II. First, the 12 anharmonic force constants alone without the third-order parameters were adjusted to give the best least squares fit to the observed data. The final set is given in Column (i) of Table II. In Columns (ii)–(v) are listed the results obtained when the anharmonic force constants were refined along with some of the third-order parameters. In addition to the 12 force constants, the parameters  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  of Eq. (8) were included and refined first. While the  $\lambda_i$ 's were supposed to have the same values for  $\text{C}^{12}\text{O}_2^{16}$  and  $\text{C}^{13}\text{O}_2^{16}$  in Set (ii), they were adjusted independently for Set (iii). The results are given in Columns (ii) and (iii); the unprimed  $\lambda$ 's are for  $\text{C}^{12}\text{O}_2^{16}$  and the primed ones for  $\text{C}^{13}\text{O}_2^{16}$ . In Column (iv) are given the results attained when  $\delta$  of Eq. (9) was included as well as the three  $\lambda$ 's, again

<sup>5</sup> The complete expressions for the third-order parameters are very complicated; Maes (14) has formulated the expressions for  $\lambda_i$  and  $\delta$  in terms of  $(3)Y$ 's; i.e., the coefficients appearing in the once transformed Hamiltonian,  $(F)h'_3$ . It is readily seen, however, that the quintic force constants in dimensionless normal coordinates,  $k_{11122}$ ,  $k_{12222}$ , and  $k_{1233a}$  contribute, respectively, to  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , while the force constant  $k_{112222}$  contributes to  $u$ .

TABLE II  
THE CONVERGED SETS OF FORCE CONSTANTS AND THIRD-ORDER PARAMETERS

	(i) f.c. <sup>a</sup>	$\sigma^b$	(ii) f.c.	$\sigma$	(iii) f.c.	$\sigma$	(iv) f.c.	$\sigma$	(v) f.c.	$\sigma$
$K_{11}$	7.9813	0.0133	7.9764	0.0110	7.9703	0.0088	8.0112	0.0024	8.0089	0.0026
$K_{13}$	1.2105	0.0239	1.1999	0.0200	1.1903	0.0105	1.2613	0.0043	1.2570	0.0054
$K_{22}$	0.3948	0.0008	0.3953	0.0007	0.3962	0.0004	0.3925	0.0002	0.3928	0.0002
$K_{111}$	-18.4823	0.1142	-18.8034	0.1298	-18.7693	0.0539	-18.9894	0.0275	-18.9483	0.0312
$K_{113}$	-1.3341	0.5994	-2.0818	0.4872	-1.8957	0.2613	-1.9545	0.1041	-1.8860	0.0851
$K_{122}$	-0.6909	0.0090	-0.5987	0.0163	-0.5961	0.0079	-0.6089	0.0033	-0.6121	0.0034
$K_{1111}$	25.4144	0.8769	28.4519	0.8031	28.5898	0.3894	26.2511	0.1653	26.1442	0.1576
$K_{1113}$	4.2400	1.1919	6.4185	1.0321	7.0201	0.5106	3.6760	0.2108	3.3291	0.2054
$K_{1133}$	3.3161	2.2324	2.3695	1.9659	3.9752	0.9733	3.0224	0.3979	2.3826	0.3123
$K_{1122}$	2.5982	0.2915	2.4358	0.2567	3.3597	0.1319	0.5037	0.0624	0.8524	0.1071
$K_{1223}$	5.8369	0.5917	6.2996	0.5043	8.1332	0.2666	1.8700	0.1243	2.5941	0.2313
$K_{2222}$	-0.0127	0.0101	-0.0264	0.0093	-0.0612	0.0050	0.0461	0.0021	0.0347	0.0035
$\lambda_1$			0.4548	0.4281	0.0235	0.2808	0.4471	0.0917	0.3583	0.1116
$\lambda_2$			0.3029	0.1609	0.4258	0.0985	0.5722	0.0386	0.4975	0.0478
$\lambda_3$			1.0274	0.3495	0.6852	0.2205	0.2475	0.0707	0.2808	0.0895
$\delta$							2.1660	0.0420	1.9657	0.0793
$\lambda'_1$					0.9663	0.2667			0.6534	0.1111
$\lambda'_2$					0.7066	0.1025			0.5089	0.0530
$\lambda'_3$					1.1695	0.2410			0.2752	0.0907
$\delta'$									1.8832	0.0765
$S^c$	151.4		111.5		25.4		4.7		3.9	

<sup>a</sup> The units of force constants are:  $\text{md}/\text{\AA}$  for  $K_{11}$  and  $K_{13}$ ,  $\text{md}\text{\AA}/\text{rad}^2$  for  $K_{22}$ ,  $\text{md}/\text{\AA}^2$  for  $K_{111}$  and  $K_{113}$ ,  $\text{md}/\text{rad}^2$  for  $K_{112}$  and  $K_{113}$ ,  $\text{md}/\text{rad}^2$  for  $K_{122}$ ,  $\text{md}/\text{\AA}^3$  for  $K_{1111}$ ,  $K_{1113}$ , and  $K_{1133}$ ,  $\text{md}/\text{\AA}\text{rad}^2$  for  $K_{1122}$  and  $K_{1223}$ , and  $\text{md}\text{\AA}/\text{rad}^4$  for  $K_{2222}$ . The third-order parameters  $\lambda$ 's are expressed in  $\text{cm}^{-1}$ , and  $\delta$  and  $\delta'$  are given in  $10^{-4}$   $\text{cm}^{-1}$ .

<sup>b</sup> The dispersions of the force constants are given in the columns indicated by  $\sigma$ .

<sup>c</sup> The sum of the squared deviations for a given set of force constants.

Table III. The Computed Values of Harmonic Frequencies ( $w_1$ ), Anharmonicity Constants ( $x_{ij}$ ) in  $\text{cm}^{-1}$ , Rotational Constants ( $a_j$ ) in  $10^{-4}\text{cm}^{-1}$ , and Force Constants in Dimensionless Normal Coordinates ( $k_{ijk}$  and  $k_{ijk\ell}$ ) in  $\text{cm}^{-1}$ .<sup>a</sup>

(a) $\text{C}^{12}\text{O}_2^{16}$	(i)	(ii)	(iii)	(iv)	(v)	G & M
$w_1$	1349.97	1349.17	1348.13	1354.31	1353.96	1354.07
$w_2$	674.85	675.21	675.99	672.85	673.17	672.95
$w_3$	2395.89	2395.66	2395.43	2396.32	2396.29	2396.30
$x_{11}$	-2.38	-2.54	-2.28	-2.93	-2.94	-3.10
$x_{12}$	1.01	0.96	3.47	-4.61	-3.64	-5.37
$x_{13}$	-18.50	-17.60	-17.56	-19.82	-19.66	-19.27
$x_{22}$	-0.23	-0.21	-0.96	1.35	1.10	1.59
$x_{23}$	-12.61	-12.93	-12.91	-12.31	-12.37	-12.51
$x_{33}$	-12.40	-12.44	-12.41	-12.47	-12.47	-12.50
$x_{2\ell 2}$	-0.38	-0.44	-0.19	-0.97	-0.88	-1.01
$a_1$	11.53	12.55	12.38	12.41	12.32	
$a_2$	-6.79	-7.37	-7.37	-7.40	-7.37	
$a_3$	30.25	30.43	30.53	30.60	30.58	
$k_{111}$	-43.53	-45.91	-45.47	-45.78	-45.56	
$k_{122}$	69.84	74.07	73.94	74.72	74.47	
$k_{133}$	-245.53	-246.57	-247.05	-249.14	-248.93	
$k_{1111}$	1.92	2.22	2.31	1.92	1.87	
$k_{1122}$	-4.85	-5.58	-3.00	-11.15	-10.13	
$k_{1133}$	18.91	21.35	21.27	19.52	19.52	
$k_{2222}$	1.20	1.38	0.88	2.45	2.27	
$k_{2233}$	-26.81	-27.97	-27.95	-27.56	-27.57	
$k_{3333}$	5.98	6.08	6.17	6.30	6.28	

<sup>a</sup> The values given in columns (i)-(v) are computed from the corresponding sets of force constants in columns (i)-(v) of Table II. The values given by Gordon and McCubbin (8) are shown in the column designated by G & M.

Table III. (Continued)

(b) C <sup>13</sup> O <sub>2</sub> <sup>16</sup>	(i)	(ii)	(iii)	(iv)	(v)
w <sub>1</sub>	1349.97	1349.17	1348.31	1354.31	1353.96
w <sub>2</sub>	655.65	655.99	656.75	653.70	653.96
w <sub>3</sub>	2327.41	2327.48	2327.26	2328.12	2328.09
x <sub>11</sub>	-2.38	-2.54	-2.28	-2.93	-2.94
x <sub>12</sub>	0.99	0.95	3.39	-4.46	-3.52
x <sub>13</sub>	-18.05	-17.17	-17.13	-19.33	-19.17
x <sub>22</sub>	-0.22	-0.20	-0.91	1.28	1.03
x <sub>23</sub>	-11.82	-12.12	-12.10	-11.54	-11.59
x <sub>33</sub>	-11.64	-11.68	-11.65	-11.71	-11.71
x <sub>2<sub>2</sub>2<sub>2</sub></sub>	-0.35	-0.41	-0.17	-0.91	-0.83
a <sub>1</sub>	11.53	12.55	12.38	12.41	12.32
a <sub>2</sub>	-6.40	-6.99	-6.98	-7.01	-6.99
a <sub>3</sub>	29.15	29.32	29.42	29.48	29.47
k <sub>111</sub>	-43.53	-45.91	-45.47	-45.78	-45.56
k <sub>122</sub>	67.86	71.96	71.85	72.60	72.36
k <sub>133</sub>	-238.54	-239.55	-240.02	-242.05	-241.84
k <sub>1111</sub>	1.92	2.22	2.31	1.92	1.87
k <sub>1122</sub>	-4.71	-5.43	-2.91	-10.83	-9.83
k <sub>1133</sub>	18.37	20.75	20.67	18.96	18.97
k <sub>2222</sub>	1.13	1.31	0.83	2.32	2.14
k <sub>2233</sub>	-25.31	-26.40	-26.38	-26.02	-26.02
k <sub>3333</sub>	5.64	5.74	5.82	5.95	5.93

isotopic invariance of both  $\lambda$ 's and  $\delta$  was assumed. This last restriction was removed in Set (v), in which a combined set of 12 anharmonic force constants, six  $\lambda$ 's and two  $\delta$ 's was refined, and the results are given in Column (v). Also included at the bottom of Table II are the weighted sum of the squared deviations:  $S = \sum_i w_i (\nu_i^{\text{obs}} - \nu_i^{\text{calc}})^2$  computed from the corresponding sets of force constants.

The calculated vibrational band centers ( $\nu_i$ ) and the differences of the effective rotational constants ( $B_v - B_0$ ) from Sets (i-v) may be obtained from the corresponding columns of Table I, where, however, only the differences between the observed and calculated values are given to save space.

In Table III are listed the harmonic frequencies ( $\omega_s$ ), anharmonic constants ( $x_{ss'}$ ), vibration-rotation coupling constants ( $\alpha_s$ ), as well as the cubic and quartic force constants in dimensionless normal coordinates ( $k_{ijk}$  and  $k_{ijkl}$ ) calculated from the corresponding sets of force constants. A number of calculations have also been made by using other combinations of third-order parameters; the results are not tabulated here but will be referred to in the following discussions.

The force constants given in Column (i) of Table II correspond to those given in Column (vi) of Table I in Ref. (1). It should be noted, however, that the present set (i) is obtained without any constraints on the values of force constants, while a few force constants were held fixed in Set (vi) of the previous paper. The reason that we have succeeded in obtaining Set (i) without any constraints is not altogether clear, since the observed data we have used here are only slightly different from those used in Ref. (1): the most recent values of Gordon and McCubbin for  $C^{12}O_2^{16}$  have replaced some of the previous data, and the relative weights of the vibrational levels to the rotational constants were increased. The latter change may have served to stabilize the normal equations.<sup>6</sup> As may be seen from Tables II and III, the inclusion of  $\lambda$ 's as adjustable parameters does not alter the values of force constants nor the fit of the calculated values to the observed too significantly, unless  $\lambda_i$ 's are taken independently for  $C^{12}O_2^{16}$  and  $C^{13}O_2^{16}$ . When six  $\lambda_i$ 's are refined as in Set (iii), the agreement between the calculated and observed frequencies is greatly improved, while that for the rotational constants is not. As a result, the sum of the squared deviations,  $S$ , has decreased from 151 to 25. However, the converged values for the six  $\lambda$ 's are not entirely satisfactory; the values of  $\lambda$ 's for  $C^{12}O_2^{16}$  are found to be far from those for  $C^{13}O_2^{16}$ , which can hardly be reconciled with the theoretical considerations. Next, the rotational third-order parameter is included, and is refined simultaneously with the 12 anharmonic force constants and three  $\lambda$ 's to obtain Set (iv), again assuming isotopic invariance for the third-order parameters. As shown in Table II, the addition of a single parameter  $\delta$  to Set (ii) has a startling effect, the value of  $S$  decreasing from 112 for Set (ii) to 4.7 for Set (iv). The vibrational energy levels and effective rotational constants computed from Set (iv) agree very well with the observed. The deviations of the calculated frequencies from the observed are less than  $1 \text{ cm}^{-1}$  for all the levels considered, including the levels

<sup>6</sup> It was rather unfortunate that the values of  $K_{1113}$  and  $K_{1133}$  were fixed at  $-2.383$  and  $-5.924 \text{ md}/\text{\AA}^3$ , respectively, which are quite different from the values obtained in the present work. This may also have caused the difficulty in obtaining a converged set without constraints.

with relatively high quantum numbers, and those for the effective rotational constants seldom exceed  $1.0 \times 10^{-4} \text{ cm}^{-1}$ . The agreement is even better for the fundamentals, first overtones, and binary combination tones, for which the effects of higher order terms such as  $y_{ss's'}$  are expected to be smaller. The average deviations are about  $0.2 \text{ cm}^{-1}$  for the vibrational levels, and  $0.2\text{--}0.3 \times 10^{-4} \text{ cm}^{-1}$  for the rotational constants. Finally, the third-order parameters  $\delta$  and  $\lambda$  are refined independently for C<sup>12</sup>O<sub>2</sub><sup>16</sup> and C<sup>13</sup>O<sub>2</sub><sup>16</sup> in Set (v), thus eight third-order parameters along with the 12 anharmonic force constants are adjusted. The converged values are given in Table II and the corresponding computed frequencies and rotational constants may be obtained from Column (v) of Table I. No significant improvement is achieved in the fit ( $S = 3.9$ ); however, it must be noted that the converged values of the third-order parameters are much more reasonable than those in Set (iii). With the exception of  $\lambda_1'/\lambda_1$ , the ratios of  $\lambda_2'/\lambda_2$ ,  $\lambda_3'/\lambda_3$ , and  $\delta'/\delta$  are quite acceptable for C<sup>13</sup>-substitution. This indicates that simultaneous refinement of  $\lambda$ 's and  $\delta$  is necessary to obtain a reasonable set of these parameters and the neglect of  $\delta$  causes the discrepancies in the values of the  $\lambda$ 's in Set (iii).<sup>7</sup> However, we feel that we may safely disregard the isotopic variances in the third-order parameters in carbon dioxide, namely  $\Delta\lambda_i = \lambda_i - \lambda_i'$  and  $\Delta\delta = \delta - \delta'$  to the present approximation. In the following discussion we will use mainly Set (iv).

Attempts were also made to include the parameter  $u$  in the refinement process. However, it was found that  $u$  neither affects the values of other parameters, nor improves the data fit too significantly. Its value is not very well determined:  $u = 0.025 \pm 0.020 \text{ cm}^{-1}$ . Therefore, the significance of  $u$  is not discussed here.

#### *Values of Force Constants*

The present calculation confirms our previous conclusions with regard to the principal diagonal force constants: the diagonal stretching potential follows closely the pattern of the Morse function for a given bond, we have  $a_1 = -K_{111}/K_{11} = 2.377$  and  $a_2 = K_{1111}/K_{11} = 3.327$ , while the Morse function predicts  $a_2^* = 7a_1^2/12 = 3.296$ . The bending potential is almost harmonic with a vanishing cubic constant and a small quartic force constant.

Only the value of  $K_{122}$  is strongly affected by the inclusion of the third-order parameters  $\lambda$ : the converged value of  $-0.69$  for Set(i) is considerably different from those found in the range of  $-0.59$  to  $-0.60$  for Sets (ii-v). The inclusion of  $\delta$  has a considerable effect upon the off-diagonal quartic force constants,  $K_{1113}$ ,  $K_{1122}$ , and  $K_{1223}$ , the values of these force constants being reduced to about one half to one sixth.

As may be seen from Table II, the values of the quadratic and cubic force constants (Set (iv)) are well determined with very small dispersions. It is in-

<sup>7</sup> We have tried to adjust  $\delta$  alone with 12 force constants, ignoring the  $\lambda$ 's, the results are not satisfactory with the value of  $S = 36$ .

interesting to note that their values also agree remarkably well with those published previously (1, 7, 15). The values of the quartic force constants, on the other hand, differ considerably from those reported earlier, this was, however, not surprising, since those values must be considered to have rather large dispersions (cf. Table I of Ref. (1)). The simultaneous refinement of the anharmonic force constants and the third-order parameters seems necessary to obtain the values of quartic force constants with reasonably small dispersions.

We may draw the potential energy map of the carbon dioxide molecule with the aid of the anharmonic force constants just obtained. In Fig. 1, we plotted the potential energy surfaces of carbon dioxide around its equilibrium position when its linearity is retained:  $R_2 = \Delta\theta = 0$ . The abscissa and ordinate correspond, respectively, to the two stretching coordinates  $r_1$  and  $r_2$ . In Fig. 2 we

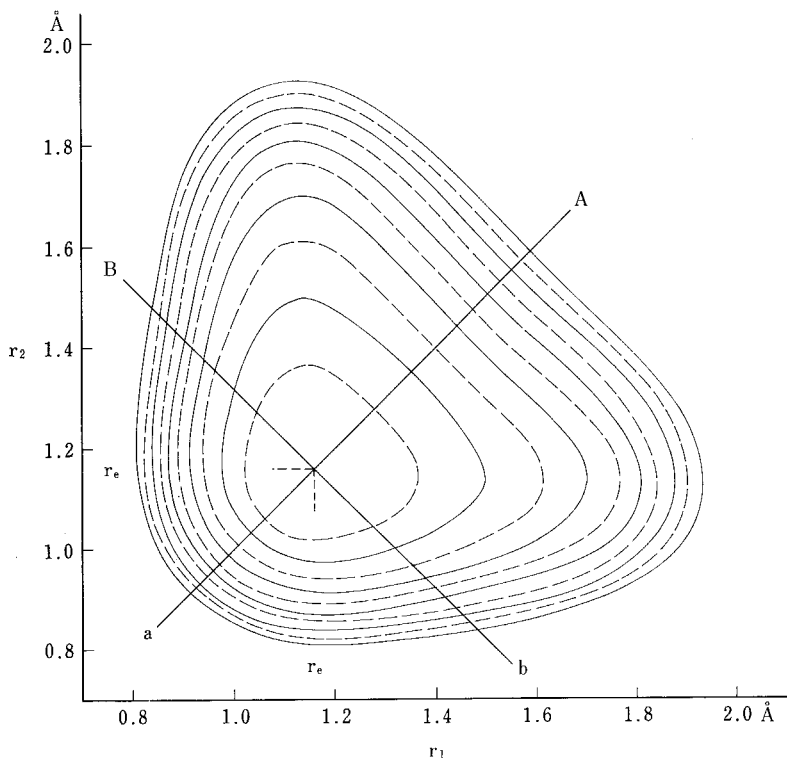


FIG. 1. Potential energy contour map of carbon dioxide around its equilibrium position. Displacement along  $r_{O-C}$  is taken as abscissa and that along  $r_{C-O}$  as ordinate, while the linearity of the molecule is retained. The contours are drawn at intervals of  $2.0 \times 10^{-12}$  erg. The equilibrium bond distances are indicated by  $r_e$ . The lines  $Aa$  and  $Bb$  represent two symmetry coordinates, i.e., the symmetric stretching ( $S_1$ ) and the antisymmetric stretching ( $S_2$ ) coordinates, respectively.



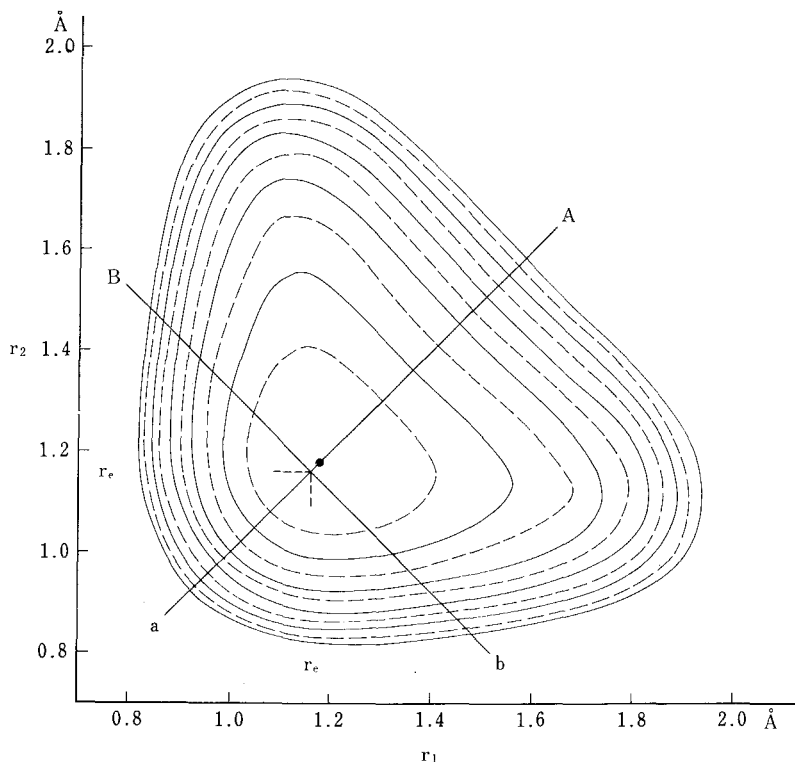


FIG. 2. Potential energy contour map of carbon dioxide, when the molecule is assumed to have a bent configuration;  $R_2 = \Delta\theta = 45^\circ$ . Displacement along  $r_{O-C}$  is taken as abscissa, and that along  $r_{C-O}$  as ordinate. The contours are drawn at intervals of  $2.0 \times 10^{-12}$  erg. The dark circle indicates the potential minimum.

plotted the potential contour map when the molecule is assumed to have a bent form:  $R_2 = \Delta\theta = 45^\circ$ . The lines  $Aa$  and  $Bb$  in the figures represent two symmetry coordinates; the symmetric stretching ( $S_1$ ) and the antisymmetric stretching ( $S_2$ ) coordinates. The general patterns of the potential energy contours are alike in both cases, except that the potential along the  $S_1$  coordinate is slightly steeper in the deformed configuration. It is also noted that the potential minimum is no longer at the origin when the molecule is in the bent configuration, but it shifts slightly toward longer bond distances (but still on the line  $Aa$ ), as indicated by the dark circle in Fig. 2. This would indicate that the two C-O bonds tend to stretch when the bending vibration is highly excited. This is further illustrated in Fig. 3, in which position of the potential minimum is plotted as a function of deviation of the valence angle from linearity:  $R_2 = \Delta\theta$ .

The dissociation energy of a C-O bond may also be evaluated from the stretch-

ing force constants,  $K_{11}$  and  $K_{111}$ , if we assume a Morse type potential. The dissociation energy  $D_e$  is related to  $K_{11}$  and  $K_{111}$  by

$$K_{11} = D_e a_1^2, \quad (12a)$$

$$K_{111} = -D_e a_1^3. \quad (12b)$$

From the values of  $8.0112 \text{ md}/\text{\AA}$  and  $-18.9894 \text{ md}/\text{\AA}^2$ , respectively, for  $K_{11}$  and  $K_{111}$ , we obtain  $D_e = 1.42 \times 10^{-11} \text{ erg} = 8.85 \text{ eV}$ . This corresponds to the dissociation of  $\text{CO}_2$  in its ground electronic state to  $\text{CO} (^1\Sigma) + \text{O} (^1D)$  but not to their ground states  $\text{CO} (^1\Sigma) + \text{O} (^3P)$  (16). In order to calculate the dissociation energy of  $\text{CO}_2$  to  $\text{O} + \text{C} + \text{O}$ , it is more convenient to use the symmetry coordinate  $S_1 = (R_1 + R_3)/\sqrt{2}$ . The force constants associated with the symmetric stretching coordinate are given as

$$F_{11} = K_{11} + K_{13}/2, \quad (13a)$$

$$F_{111} = (K_{111} + K_{113})/\sqrt{2}, \quad (13b)$$

$$F_{1111} = (2K_{1111} + 2K_{1113} + K_{1133})/4. \quad (13c)$$

Their values are, respectively,  $8.642 \text{ md}/\text{\AA}$ ,  $-14.809 \text{ md}/\text{\AA}^2$ , and  $15.719 \text{ md}/\text{\AA}^3$ .

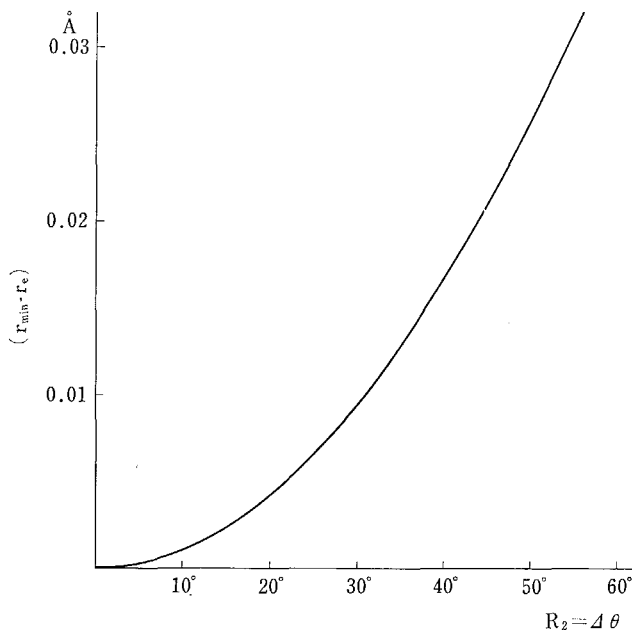


FIG. 3. The potential energy minimum as a function of the angle bending coordinate  $R_2 = \Delta\theta$ . The displacement of the potential minimum from its equilibrium ( $r_{\min} - r_e$ ) is drawn for a given bending coordinate  $\Delta\theta$ .

It is readily seen that the potential energy along the symmetry coordinate  $S_1$  also follows closely the Morse function. We find  $b_1 = -F_{111}/F_{11} = 1.714$  and  $b_2 = F_{1111}/F_{11} = 1.819$ , while the Morse type potential predicts the value of  $b_2^* = 7b_1^2/12 = 1.713$ . The estimated value of  $D_e$  in this case is around 18 eV, which is not far from the value of 16.54 eV (381.54 kcal/mol) determined thermodynamically (17).<sup>8</sup>

### Unperturbed Energy Levels

The unperturbed vibrational energy levels and rotational constants are computed from Set (iv). The values for a few typical polyads are given in Table IV. The computed value for  $E_{100}^0$  is actually lower than that of  $E_{0200}^0$  in accordance with the latest vibrational analysis (5, 6). It is also worth mentioning that the unperturbed levels of C<sup>13</sup>O<sub>2</sub><sup>16</sup> in some polyads are also very close, the last tetrad in Table IV being an example. This may be the reason that  $\delta$  and  $\delta'$  in Set (v) are determined with almost equal uncertainties.

### Application to O<sup>18</sup>-Substituted Carbon Dioxide

As pointed out earlier, the anharmonic force constants are invariant to isotopic substitutions. We are now able to compute the vibrational and rotational constants for any isotopic species of carbon dioxide, once the force constants have been determined with reasonable accuracy. This has been done for C<sup>12</sup>O<sup>16</sup>O<sup>18</sup> and C<sup>13</sup>O<sup>16</sup>O<sup>18</sup>, and the computed constants are given in Table V. Several vibrational levels and their rotation constants were reported for these species (8, 9, 18), and the calculated values are compared with the observed in Table VI. The agreement is generally very good. This shows that the vibrational levels and rotation constants of C<sup>12</sup>O<sup>16</sup>O<sup>18</sup> and C<sup>13</sup>O<sup>16</sup>O<sup>18</sup> can be explained satisfactorily from the sets of constants,  $\omega_s$ ,  $x_{ss'}$ ,  $W_e$ , and  $\alpha_s$  from the levels of C<sup>12</sup>O<sub>2</sub><sup>16</sup> and C<sup>13</sup>O<sub>2</sub><sup>16</sup>. In Table VII, we summarize the values of Fermi coupling constants for five isotopic species of carbon dioxide.

Berney and Eggers (18) considered the possibility of Fermi resonance between  $(2\nu_1)^0$  and  $\nu_3^0$  for O<sup>18</sup>-substituted molecules. Both levels belong to the same symmetry species, because of the lower symmetry of the molecule ( $C_{\infty v}$ ) and  $k_{113}$  is no longer zero. However, the computed value of  $k_{113}$  is  $-4.46 \text{ cm}^{-1}$  for C<sup>12</sup>O<sup>16</sup>O<sup>18</sup>, very different from the estimated value given by these authors ( $11.45 \text{ cm}^{-1}$ ). The vibrational band centers do not seem to be affected by this kind of resonance more than  $0.02 \text{ cm}^{-1}$ .

<sup>8</sup> This value obtained from the following relations:

CO <sub>2</sub> (g) = CO(g) + 1/2O <sub>2</sub> (g)	66.77 kcal/mol
1/2O <sub>2</sub> (g) = O	58.58 kcal/mol
CO(g) = C + O	256.19 kcal/mol
Total	381.94 kcal/mol

TABLE IV

THE CALCULATED UNPERTURBED AND PERTURBED LEVELS (IN  $\text{CM}^{-1}$ ) AND ROTATIONAL CONSTANTS (IN  $10^{-5} \text{CM}^{-1}$ ) FROM SET (IV) FOR SOME POLYADS

Level	$(E_v)^0$	$E_v$	$E_{\text{obs}}$	$(B_v)^0$	$B_v$	$B_{\text{obs}}$
(a) $\text{C}^{12}\text{O}_2^{16}$						
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2^0 & 0 \end{bmatrix}$	1333.94	1388.01	1388.19	38897	39019	39020
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2^0 & 0 \end{bmatrix}$	1339.67	1285.60	1285.41	39169	39047	39048
$\begin{bmatrix} 2 & 0 & 1 \\ 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	4971.54	5099.42	5099.61	38467	38752	38751
$\begin{bmatrix} 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	4969.11	4977.82	4977.81	38739	38650	38654
$\begin{bmatrix} 0 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	4990.15	4853.58	4853.63	39011	38816	38818
$\begin{bmatrix} 3 & 0 & 1 \\ 2 & 2^0 & 1 \\ 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6273.94	6502.81	6503.05	38343	38804	38798
$\begin{bmatrix} 2 & 2^0 & 1 \\ 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6268.15	6348.26	6347.81	38615	38648	38644
$\begin{bmatrix} 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6285.83	6228.15	6227.88	38887	38665	38668
$\begin{bmatrix} 0 & 6^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6326.98	6075.69	6075.93	39159	38887	38868
(b) $\text{C}^{13}\text{O}_2^{16}$						
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2^0 & 0 \end{bmatrix}$	1334.33	1370.23	1370.05			
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2^0 & 0 \end{bmatrix}$	1301.65	1265.75	1265.81			
$\begin{bmatrix} 2 & 0 & 1 \\ 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	4907.65	4991.47	4991.31	38480	38667	38667
$\begin{bmatrix} 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	4868.16	4887.35	4887.35	38744	38681	38681
$\begin{bmatrix} 0 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	4850.92	4747.91	4748.01	39009	38886	38881
$\begin{bmatrix} 3 & 0 & 1 \\ 2 & 2^0 & 1 \\ 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6210.94	6363.77	6363.58	38355	38700	38701
$\begin{bmatrix} 2 & 2^0 & 1 \\ 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6168.38	6242.40	6241.93	38620	38592	38583
$\begin{bmatrix} 1 & 4^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6148.07	6119.85	6119.56	38884	38754	38756
$\begin{bmatrix} 0 & 6^0 & 1 \\ 0 & 6^0 & 1 \end{bmatrix}$	6150.00	5951.41	5951.53	39149	38964	38963

TABLE V

THE COMPUTED VIBRATIONAL AND ROTATIONAL CONSTANTS, THE CUBIC AND QUARTIC FORCE CONSTANTS IN DIMENSIONLESS NORMAL COORDINATES FOR  $\text{C}^{12}\text{O}^{16}\text{O}^{18}$  AND  $\text{C}^{13}\text{O}^{16}\text{O}^{18}$  (IN  $\text{CM}^{-1}$ )

	$\text{C}^{12}\text{O}^{16}\text{O}^{18}$	$\text{C}^{13}\text{O}^{16}\text{O}^{18}$		$\text{C}^{12}\text{O}^{16}\text{O}^{18}$	$\text{C}^{13}\text{O}^{16}\text{O}^{18}$
$w_1$	1315.21	1315.13	$k_{111}$	-43.85	-43.86
$w_2$	667.72	648.42	$k_{122}$	73.01	70.88
$w_3$	2378.53	2309.85	$k_{133}$	-243.33	-236.24
$x_{11}$	-2.76	-2.76	$k_{113}$	-4.46	-4.78
$x_{12}$	-4.45	-4.30	$k_{223}$	-6.50	-6.67
$x_{13}$	-19.04	-18.55	$k_{333}$	7.87	8.21
$x_{22}$	1.34	1.26	$k_{1111}$	1.81	1.81
$x_{23}$	-12.18	-11.41	$k_{1122}$	-10.73	-10.42
$x_{33}$	-12.34	-11.59	$k_{1133}$	18.77	18.22
$x_{1212}$	-0.95	-0.90	$k_{2222}$	2.42	2.28
$\alpha_1 \times 10^4$	11.38	11.38	$k_{2233}$	-25.64	-25.65
$\alpha_2 \times 10^4$	-7.03	-6.67	$k_{3333}$	6.22	5.87
$\alpha_3 \times 10^4$	28.79	27.70			

Three quartic force constants, i.e.,  $k_{1333}$ ,  $k_{1113}$ , and  $k_{1223}$  are not zero in these molecules, but they do not contribute to  $E_v/hc$ .

TABLE VI  
THE OBSERVED AND CALCULATED VIBRATIONAL LEVELS (CM<sup>-1</sup>) AND THEIR  
ROTATIONAL CONSTANTS (10<sup>-4</sup> CM<sup>-1</sup>) FOR C<sup>12</sup>O<sup>16</sup>O<sup>18</sup> AND C<sup>13</sup>O<sup>16</sup>O<sup>18</sup>

$v_1 v_2^l v_3$	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	$(B_v - B_0)_{\text{obs}}$	$(B_v - B_0)_{\text{calc}}$
(a) C <sup>12</sup> O <sup>16</sup> O <sup>18</sup>				
$\begin{bmatrix} 2 & 0 & 0 \\ 1 & 2^0 & 0 \\ 0 & 4^0 & 0 \end{bmatrix}$	2757.14	2755.79	9.0	9.2
	2614.20	2614.60	-4.3	-4.4
	2500.73	2501.69	2.5	3.2
$\begin{bmatrix} 2 & 0 & 1 \\ 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	5042.54	5041.61	-20.7	-20.3
	4904.85	4904.88	-33.55	-33.55
	4791.26	4791.82	-24.5	-24.4
$\begin{bmatrix} 1 & 1^1 & 0 \\ 0 & 3^1 & 0 \end{bmatrix}$	2049.68	2048.66		
	1901.90	1902.46		
$\begin{bmatrix} 1 & 0 & 1 \\ 0 & 2^0 & 1 \end{bmatrix}$	3675.13	3674.74	-26.09	-25.99
	3571.14	3571.41	-28.78	-28.84
0 0 1	2332.16	2332.15	-28.70	-28.76
0 0 2	4639.48	4639.61	-57.80	-57.52
(b) C <sup>13</sup> O <sup>16</sup> O <sup>18</sup>				
$\begin{bmatrix} 2 & 0 & 1 \\ 1 & 2^0 & 1 \\ 0 & 4^0 & 1 \end{bmatrix}$	4924.99	4924.38	-27.0	-27.2
	4814.53	4814.58	-33.3	-33.6
	4692.12	4692.12	-16.3	-16.4
$\begin{bmatrix} 1 & 0 & 1 \\ 0 & 2^0 & 1 \end{bmatrix}$	3587.51	3587.32	-29.0	-30.0
	3490.35	3490.57	-22.7	-22.7
0 0 1	2265.98	2266.00	-28.3	-27.7

TABLE VII  
FERMI COUPLING CONSTANTS  $W_e$

	$W_e = -k_{122}/\sqrt{2} \text{ cm}^{-1}$
C <sup>12</sup> O <sub>2</sub> <sup>16</sup>	-52.84
C <sup>13</sup> O <sub>2</sub> <sup>16</sup>	-51.34
C <sup>12</sup> O <sup>16</sup> O <sup>18</sup>	-51.63
C <sup>13</sup> O <sup>16</sup> O <sup>18</sup>	-50.12
C <sup>12</sup> O <sub>2</sub> <sup>18</sup>	-50.52

### CONCLUSION

It has been shown that a reasonable set of constants in the general quartic force field of carbon dioxide can be obtained by the least squares method, provided that the third-order parameters,  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ , and  $\delta$  in the Fermi coupling off-diagonal elements are refined simultaneously with the force constants. Vibrational band centers and effective rotational constants have been computed from the converged set, Set (iv), of force constants and third-order parameters. Excellent agreement between the calculated values and the corresponding experimental

values is found for both  $C^{12}O_2^{16}$  and  $C^{13}O_2^{16}$ , the average deviations being  $0.2\text{ cm}^{-1}$  for the vibrational levels and  $0.3 \times 10^{-4}\text{ cm}^{-1}$  for the rotational constants. It has also been shown that the vibrational levels and rotational constants of  $C^{12}O^{16}O^{18}$  and  $C^{13}O^{16}O^{18}$  are accounted for by Set (iv), although the fit is slightly inferior to that for  $C^{12}O_2^{16}$  and  $C^{13}O_2^{16}$ ; this was expected since the observational data for  $C^{12}O^{16}O^{18}$  and  $C^{13}O^{16}O^{18}$  were not included in the refinement process. This would indicate that a further improvement in the values of the anharmonic force constants can be expected, if highly precise measurements of appropriate vibration-rotation bands are made for  $C^{12}O^{16}O^{18}$  and  $C^{13}O^{16}O^{18}$ .

The anharmonic force constants also serve to give a quantitative picture of potential energy surfaces, especially around the equilibrium position of the carbon dioxide molecule; the stretching diagonal force constants are shown to be represented well by the Morse function. An estimate of the dissociation energy from the values of quadratic and cubic force constants by assuming the Morse function has been made with fair success.

It is believed that the present results confirm the validity and usefulness of our method, since a large number of spectroscopic data of various isotopic species of carbon dioxide are interpreted satisfactorily in terms of 16 basic parameters of the molecule, namely 12 anharmonic force constants and four third-order parameters.

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