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The 2.8-Micron Bands of CO_2*

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The spectrum of CO_2 has been measured at 2.8 microns using an echelle grating-prism spectrometer. Ten bands of $C^{12}O_2^{16}$, one band of $C^{13}O_2^{16}$, and two bands of $C^{12}O^{16}O^{18}$ were measured with an accuracy of ± 0.005 cm^{-1} for individual lines. The measurements, when combined with those at 15 microns, allowed a complete vibrational analysis to be carried out to second order for $C^{12}O_2^{16}$. It has been verified that the unperturbed 02^00 level is above the 10^00 level and a value of $\delta = 2.5 \pm 0.1 \times 10^{-4}$ cm^{-1} has been determined.

INTRODUCTION

The strong 10^01–000 and 02^01–000 combination bands of CO_2 and the "hot" bands associated with it occur in the 2.8-micron region of the spectrum. Recent high resolution studies of these spectra have been made by Jones and Bell (*1*), Benedict and Plyler (*2*), France and Dickey (*3*), Rossmann, France, Rao, and Nielsen (*4*) and Courtoy (*5, 6*). These remeasurements of some of the bands studied by Courtoy have been undertaken because it makes possible a precise verification of the recent calculations of Amat and Pimbert (*7*) who showed how to analyze the vibrational spectrum of CO_2 without using an incorrect relationship among the rotational constants and the separations of levels in Fermi resonance. Other recent research about the vibrational spectrum of CO_2 has been described by Berney and Eggers (*8*), and by Pariseau *et al.* (*9*).

Courtoy's very extensive investigations were made shortly before the development of the interferometric and echelle techniques of wavelength measurement. Remeasurements made in this laboratory indicate that Courtoy's measurements show a remarkably high degree of relative accuracy within a band but that the absolute frequencies in the 3500- to 3700-cm^{-1} region are consistently low by about 0.03 cm^{-1}. Our Δ_2F'' values are in perfect agreement with those of Courtoy but exhibit somewhat smaller observed minus computed differences. Therefore extensive use has been made of Δ_2F values computed from Courtoy's

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B_{000} and D_{000}. The measurements indicate that the value of $B_{000} = 0.39021$ cm^{-1} is probably somewhat more accurate than $\pm 4 \times 10^{-5}$ cm^{-1} as claimed by Courtoy. The band origins, ΔB values, and ΔD values of the 10^01–000 and 02^01–000 bands determined from the present research are also in excellent agreement with the measurements of Rossmann, France, Rao, and Nielson.

The objective of the present study is to measure constants of the 2.8-micron bands and combine them with our 15 micron measurements (*10*) to derive a set of second-order vibrational constants using the method of Amat and Pimbert.

TABLE I

Calculated and Observed Wave Numbers in the 10^01–00^00 Band of $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O−C	R(J) (Calc.)	O−C
0			3715.556	−1
2	3713.215	−1	17.085	1
4	11.622	0	18.589	−4
6	10.005	−1	20.068	−1
8	08.362	1	21.521	−2
10	06.695	−2	22.950	0
12	05.002	2	24.353	−1
14	03.284	5	25.730	
16	01.541	1	27.083	1
18	3699.774	3	28.410	2
20	97.982	−1	29.712	3
22	96.165	8	30.989	−1
24	94.324	0	32.241	
26	92.458	19	33.468	
28	90.568		34.671	
30	88.654	−4	35.848	3
32	86.715	−4	37.000	−3
34	84.753	−3	38.128	6
36	82.767	−4	39.232	5
38	80.757	0	40.311	8
40	78.724		41.365	2
42	76.668	0	42.396	2
44	74.588	−1	43.402	7
46	72.486	0	44.385	6
48	70.361	2	45.343	6
50	68.213	−3	46.278	
52	66.042	14	47.190	
54	63.850	0	48.078	
56	61.636	12	48.943	−1
58	59.400	2	49.785	10
60	57.143	11	50.605	17
62	54.864	1	51.401	
64	52.565	4	52.176	

EXPERIMENTAL PROCEDURE

Ten bands of $C^{12}O_2^{16}$ which occur in the spectral region between 3546 and 3758 cm^{-1}, two bands of $C^{12}O^{16}O^{18}$, and one band of $C^{13}O_2^{16}$ have been measured using a 2.5-meter grating prism vacuum spectrometer (*11*). The radiation source was a 100-watt zirconium arc operated with a water jacket in the vacuum chamber. The detector was a lead sulfide cell cooled with liquid nitrogen. A 30-line-per-mm echelle was used doubly passed in the 22nd and 23rd orders to observe the CO_2 spectrum with the spectrometer serving as a 24-meter absorption cell. Lines in the 2–0 band of CO, which have been measured by Rank, Skorinko, Eastman, and Wiggins (*12*), served as wavelength standards. The method of measurement was to make a preliminary trace of the standard lines to desermine their counter numbers on the wavelength drive. Standard lines were observed in the 25th, 26th, and 27th orders. The prism was then adjusted to record the CO_2

TABLE II

Calculated and Observed Wave Numbers in the 02^01–00^00 Band of $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3613.618	−3
2	3611.278	−1	15.153	−6
4	9.690	−5	16.665	−3
6	8.080	−2	18.155	2
8	6.449	−3	19.623	−6
10	4.796	−6	21.069	6
12	3.121	−4	22.493	6
14	1.425	6	23.895	7
16	3599.706	−4	25.275	14
18	97.966	−5	26.633	9
20	96.205	10	27.968	6
22	94.421	−5	29.281	5
24	92.615	−1	30.571	4
26	90.787	−4	31.838	3
28	88.937	−3	33.082	−1
30	87.065	−1	34.303	0
32	85.170	−4	35.501	2
34	83.253	−2	36.675	8
36	81.313	3	37.825	7
38	79.351	1	38.952	0
40	77.366	1	40.055	3
42	75.357	−2	41.133	4
44	73.325		42.187	5
46	71.270	6	43.215	2
48	69.191	3	44.219	−3
50	67.089	5	45.198	6
52	64.962	5	46.151	

spectrum, and with the grating drive motor and recorder always running, the prism was retuned to record each standard line. A second CO_2 spectrum was recorded without interruptions so that all CO_2 lines could be observed. Several measurements were made of most of the lines.

DETERMINATION OF THE CONSTANTS

Eight of the bands were sufficiently complete so that their constants could be determined by a least squares fit of the data to the equation

$$R(J) + P(J) = 2(\nu_0 + B') + 2(B' - B'')J(J + 1) - 2(D' - D'')J^2(J + 1)^2. \quad (1)$$

About a fourth of the lines could not be measured because of blends. The frequencies for these lines were calculated using $\Delta_2 F$ values.

TABLE III

Calculated and Observed Wave Numbers in the 11^11–01^10 (c–c) Band of $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
1			3724.793	1
3	3720.887	−2	26.310	−2
5	19.278	−3	27.800	
7	17.644	1	29.264	−1
9	15.983	−1	30.702	−1
11	14.297	−4	32.114	
13	12.584	1	33.499	
15	10.846	−13	34.858	5
17	9.081	0	36.191	8
19	7.291	3	37.498	2
21	5.475	−13	38.778	2
23	3.633	1	40.032	−8
25	1.766		41.260	
27	3699.873	−6	42.462	−1
29	97.955		43.637	8
31	96.011		44.786	
33	94.042	3	45.910	3
35	92.047	2	47.007	2
37	90.028	−2	48.078	
39	87.983	−1	49.123	3
41	85.914	10	50.142	
43	83.819		51.136	
45	81.700	2	52.103	
47	79.556		53.045	9
49	77.388	10	53.961	16
51	75.195	−5	54.851	

The 12^01–10^00, 12^01–02^00, 04^01–02^00, and 04^21–02^20 bands were too incomplete to form enough of the $R(J) + P(J)$ combinations for analysis. The lines in these bands were used in the equation

$$\nu = \nu_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 - 2(D' + D'')m^3 - (D' - D'')m^4 \tag{2}$$

to determine ν_0 and $B' - B''$. The quantities $B' + B''$, $D' + D''$, and $D' - D''$ were not determined by fitting the polynomial. They were computed from Courtoy's values of upper-state rotational constants and from values of lower-state constants derived in this laboratory from 15-micron measurements. This

TABLE IV

Calculated and Observed Wave Numbers in the 11^11–01^10 (d–d) Band of $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3724.026	
2	3721.679	−4	25.561	4
4	20.084	−4	27.072	0
6	18.464	1	28.558	0
8	16.821	−5	30.020	0
10	15.154	−1	31.458	2
12	13.462	−3	32.871	2
14	11.747	1	34.261	
16	10.007		35.626	
18	8.244		36.967	
20	6.458	0	38.284	6
22	4.647	10	39.576	
24	2.814	1	40.845	
26	0.956	4	42.090	5
28	3699.076	8	43.311	8
30	97.172	−5	44.508	
32	95.245	2	45.681	6
34	93.295	0	46.831	5
36	91.323		47.957	6
38	89.328	4	49.059	9
40	87.310		50.139	
42	85.270		51.195	
44	83.208		52.227	
46	81.124	0	53.237	4
48	79.018		54.224	6
50	76.891	−5	55.189	3
52	74.742		56.130	2
54	72.572		57.050	
56	70.381		57.947	−2
58	68.169		58.821	0

TABLE V

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 03^11–01^10 (c–c) BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
1			3581.871	−1
3	3577.965	−1	83.394	
5	76.363	−3	84.893	
7	74.737	3	86.370	−4
9	73.089	1	87.824	
11	71.418	3	89.254	1
13	69.725		90.662	2
15	68.008	−2	92.046	7
17	66.269	9	93.407	
19	64.507	1	94.744	1
21	62.722	1	96.059	−1
23	60.914		97.349	−1
25	59.083	7	98.617	−9
27	57.230	5	99.860	−2
29			3601.080	
31			2.276	1
33			3.448	3
35			4.596	0
37			5.720	−2
39			6.819	
41			7.894	
43			8.945	2
45			9.971	6
47			10.972	
49			11.948	8
51			12.899	4
53			13.825	5

procedure yields the precise values of the band centers needed for the analysis and fairly good values of ΔB.

Tables I through XVI give the calculated lines and values of observed minus calculated frequencies for all of the 2.8-micron bands. Table XVII gives all of the band centers and ΔB and ΔD values used in the analysis.

ANALYSIS

Ten constants in the second-order expression for the unperturbed energy levels

$$E_v^0 = \sum_i \omega_i^0 v_i + \sum_{ij} x_{ij} v_i v_j + g_{22} l_2^2 \tag{3}$$

must be determined. Fermi resonance, to the second order of approximation, introduces the cubic potential constant k_{122}. Amat and Pimbert (7) have shown

TABLE VI

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 03^11–01^10 (d–d) BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
2	3578.757	3	3582.644	1
4	77.166		84.163	
6	75.556	−1	85.661	−2
8	73.924	2	87.139	
10	72.273	2	88.596	
12	70.601	0	90.033	−1
14	68.908	0	91.449	
16	67.196	4	92.844	1
18	65.462	5	94.218	−1
20	63.709	1	95.571	−4
22	61.935		96.903	0
24	60.140		98.214	
26	58.325	6	99.503	9
28	56.489	2	3600.771	−3
30	54.632	−1	2.018	1
32	52.755		3.242	−1
34	50.857	0	4.445	
36	48.938		5.626	−1
38	46.997	2	6.785	
40			7.921	
42			9.036	−1
44			10.127	1
46			11.196	5
48			12.242	
50			13.264	−6

that observable unperturbed energy levels and sums of levels in Fermi resonance can be used to evaluate six of the ten constants and three linearly independent combinations of the other four. The first column of Table XVIII is a list of the values of the directly observable constants and combinations of constants obtained from the bands in Table XVII.

The traditional approach to the problem of evaluation of the ω's, x's, and k_{122} has been to calculate Δ_0, the unperturbed separations of levels in Fermi resonance, by means of the relationship

$$\Delta B = (\Delta_0/\Delta)\Delta B_0 . \qquad (4)$$

Δ, the perturbed energy level separation and ΔB and ΔB_0, the perturbed and unperturbed rotational constants are readily observable. Knowing Δ_0, one can use an additional relationship among the ω's and x's to evaluate all of these constants. k_{122} can be calculated from the well-known secular equation

TABLE VII

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 12^21–02^20 (c–c) BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
2			3728.194	
4	3723.475		29.717	
6	21.852		31.953	3
8	20.204		33.413	
10	18.531		34.848	
12	16.833		36.257	−2
14	15.110	−3	37.641	1
16	13.363	−5	39.001	3
18	11.590	2	40.334	1
20	9.793	1	41.643	1
22	7.971	1	42.927	−1
24	6.125	−4	44.185	
26	4.254		45.418	
28	2.358	−3	46.626	−7
30	0.438	−7	47.808	−10
32	3698.494	−13	48.966	
34			50.099	−6

TABLE VIII

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 12^21–02^20 (d–d) BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
3	3724.277		3729.717	
5	22.667	−6	31.214	0
7	21.031	4	32.686	9
9	19.371	−2	34.134	2
11	17.685		35.556	
13	15.975		36.953	
15	14.240		38.324	
17	12.480	−5	39.671	
19	10.695		40.992	4
21	8.885	1	42.288	5
23	7.051	5	43.559	10
25	5.192	−6	44.805	
27	3.309		46.025	1
29	1.401		47.220	
31	3699.469	4	48.391	2
33	97.512	−7	49.536	−1
35	95.531	0	50.656	10
37	93.526	10	51.751	3
39			52.821	
41			53.866	
43			54.886	
45			55.881	7
47			56.851	8

TABLE IX

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 04^21–02^20 BAND OF $C^{12}O_2^{16}$

J	$R(J)$ (Calc)	O − C
7	3558.938	22
8	59.663	3
12	62.551	−8
13	63.257	−3
14	63.957	9
16	65.342	5
17	66.026	−15
19	67.379	−2
21	68.708	−2
23	70.016	−10
27	72.566	22

TABLE X

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 20^01–10^00 BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3712.250	
2	3709.909		13.784	−9
4	8.321		15.296	
6	6.712		16.787	
8	5.081		18.256	4
10	3.429	−8	19.703	−6
12	1.756		21.129	5
14	0.061	5	22.534	5
16	3698.345	2	23.917	4
18	96.608	0	25.278	1
20	94.850		26.618	
22	93.071	−14	27.937	
24	91.271		29.234	
26	89.450		30.509	
28	87.609		31.764	
30	85.747	1	32.997	
32	83.864		34.210	
34	81.962		35.401	8
36	80.039	8	36.572	−7
38	78.096	4		

$$\Delta^2 = \Delta_0^2 + 4\langle W_{12}^2\rangle \tag{5}$$

and the equation for the matrix elements, which for a diad is

$$\langle W_{12}\rangle = (-k_{122}/2\sqrt{2})[(v_2 + 2)^2 - l^2]^{1/2}. \tag{6}$$

Such an analysis leads to constants which accurately predict energy levels but which do not yield values of $\langle W_{12}\rangle$ which obey isotopic substitution relation-

TABLE XI

CALCULATED AND OBSERVED WAVE NUMBERS IN THE $12^{0}1$–$10^{0}0$ BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Cacl)	O − C	$R(J)$ (Calc)	O − C
10			3597.747	−1
12	3579.800	2		
14	78.057	−2		
16	76.284	4	3601.793	−2
20	72.653	0	04.339	−2
22	70.794	4		

TABLE XII

CALCULATED AND OBSERVED WAVE NUMBERS IN THE $12^{0}1$–$02^{0}0$ BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Cacl)	O − C	$R(J)$ (Calc)	O − C
6			3697.662	−7
10	3684.253	−9		
18	77.159	10	3705.755	1
20	75.309	4	06.995	10
24	71.515	3		
26			10.522	−1
30			12.721	−2
34	61.499	1	14.797	−4
36			15.787	−1

TABLE XIII

CALCULATED AND OBSERVED WAVE NUMBERS IN THE $04^{0}1$–$02^{0}0$ BAND OF $C^{12}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
4			3572.053	−11
10			76.504	4
12	3558.544	6		
14	56.868	6		
20	51.728	−13	83.547	1
24			86.230	−4
26	48.210	4	87.544	4
30			90.106	6

ships. Furthermore, a valid relationship between the x's and ω's and k_{122} yields an imaginary value of k_{122}. Amat and Pimbert show that these inconsistencies are the result of the omission from the right-hand side of Eq. (4) of a term $4\langle W_{12}\rangle\delta/\Delta$, where δ is an unknown constant. They solve the problem by means of two relationships between the quantity $x_{12} - 4x_{22}$ and k_{122}. The first of these

TABLE XIV

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 10^01–00^00 BAND OF $C^{12}O^{16}O^{18}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3571.874	
1	3570.407		72.599	
2	69.664		73.318	
3	68.917		74.031	
4	68.163		74.739	
5	67.403		75.440	
6	66.638		76.136	
7	65.867	9	76.827	
8	65.091	−2	77.511	−2
9	64.308	5	78.190	−6
10	63.520		78.863	−2
11	62.726		79.530	0
12	61.927		80.191	−10
13	61.121		80.846	2
14	60.310	3	81.496	5
15	59.493	2	82.139	
16	58.671	2	82.777	3
17	57.842		83.409	−15
18	57.008	7	84.035	
19	56.168		84.655	
20	55.322		85.269	14
21	54.471	−12	85.878	−9
22	53.613		86.480	
23	52.750		87.076	
24	51.881		87.667	
25	51.006	−14	88.251	0
26	50.126	6	88.830	
27	49.239	8	89.402	−2
28			89.968	
29			90.529	−4
30			91.083	−3
31			91.631	
32			92.173	−10

relationships, which leads to the curve of an ellipse, is obtained by calculating Δ_0 in terms of ω_i's and x_{ij}'s from Eq. (3) and inserting Δ_0^2 in Eq. (5). The second relationship is the one between k_{122} and anharmonic constants, derived from the quantum mechanical calculation for the energy levels of a linear triatomic molecule. This relation is a parabolic curve. The elliptical curves for the Σ diads and the parabolic curve plotted in Fig. 1 show that $x_{12} - 4x_{22} = -11.70 \text{ cm}^{-1} \pm 0.1 \text{ cm}^{-1}$. Ellipses for the two Σ diads were used instead of the curves for all five diads because the Σ diads exhibit the smallest Taylor–Benedict–Strong effect

TABLE XV

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 02^01–00^00 BAND OF $C^{12}O^{16}O^{18}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3675.861	
1	3674.394		76.587	
2	73.652		77.308	5
3	72.905		78.023	−6
4	72.153	4	78.734	
5	71.396	1	79.439	
6	70.633		80.139	−3
7	69.866		80.833	
8	69.093	−1	81.523	
9	68.315		82.207	6
10	67.531		82.886	−2
11	66.743	−1	83.560	2
12	65.950		84.228	
13	65.151		84.891	0
14	64.347	9	85.549	1
15	63.539		86.202	7
16	62.724	3	86.850	−1
17	61.905	4	87.493	
18	61.081	9	88.130	2
19	60.252	−3	88.762	
20	59.417		89.389	
21	58.578	−3	90.011	
22	57.733	0	90.628	
23	56.883		91.239	
24	56.029	0	91.845	
25	55.169	−10	92.447	
26	54.304	0	93.043	
27	53.435	−4	93.634	3
28	52.560		94.220	
29	51.680	−1	94.801	6
30	50.796		95.376	4
31	49.906	−2		

(13, 14). The value of $x_{12} - 4x_{22}$ was used to evaluate the four constants in the second column of Table XVIII.

A further refinement to the calculation of k_{122} may be made by including the Taylor–Benedict–Strong effect. The value of the Fermi coupling energy for diads, which according to Eq. (6) depends only upon v_2 and ℓ, actually is slightly dependent upon the other quantum numbers and undetermined constants λ_1, λ_2, and λ_3. We have used the vibrational constants in Table XVIII to calculate values of Δ_0 and $\langle W_{12}\rangle$ for each of the five resonating diads. Knowing the value of $\langle W_{12}\rangle$, one can calculate the values of $k_{122} - \sqrt{2}\lambda_1$, λ_2, and λ_3. The

TABLE XVI

CALCULATED AND OBSERVED WAVE NUMBERS IN THE 10^01–00^00 BAND OF $C^{13}O_2^{16}$

J	$P(J)$ (Calc)	O − C	$R(J)$ (Calc)	O − C
0			3633.690	−3
2	3631.349	−1	35.216	
4	29.753		36.714	
6	28.128	0	38.183	−8
8	26.476	8	39.624	−5
10	24.796	1	41.037	1
12	23.087	19	42.421	−2
14	21.351	4	43.778	1
16	19.586		45.106	0
18	17.794	−11	46.406	
20	15.975	−7	47.678	
22	14.127		48.922	
24	12.253	−7	50.138	0
26	10.350	0	51.325	
28	8.421	−2	52.485	0
30	6.464		53.617	−2
32	4.480		54.721	−2
34	2.469	13	55.798	−3
36	0.431	−2	56.847	
38			57.868	
40			58.862	2
42			59.828	0
44			60.768	−3
46			61.680	
48			62.565	0
50			63.424	0

values are 74.52, 0.66, and 0.29 cm^{-1}. It would be necessary to study a pair of Fermi triads in order to evaluate λ_1.

Table XIX is a list of the values of $\langle W_{12}\rangle$ obtained using Eq. (5), the observed values of Δ, and the calculated values of Δ_0. Shown for comparison are the values of $\langle W_{12}\rangle$ calculated using $k_{122} - \sqrt{2}\lambda_1$, λ_2, and λ_3 in the equation for the Taylor–Benedict–Strong effect.

The first- and second-order vibrational constants from Table XVIII and the Fermi coupling energies can be used to compute the observed energy levels, as listed in Table XX. The inaccuracy of the value of $x_{12} - 4x_{22}$ and the neglect of the higher order terms probably is the reason that most of the observed energy levels are a few hundredths of one cm^{-1} smaller than the calculated values.

It would of course be possible to gain agreement either by adjusting the ω_i^0's and x_{ij}'s or by including some third-order constants, but we do not believe

TABLE XVII

VALUES OF ν_0, ΔB, AND ΔD FOR THE CO_2 BANDS MEASURED OR USED

Molecule	Band	ν_0	B'-B" x 10^5 cm^{-1}	D'-D" x $10^8 cm^{-1}$	$q' x 10^5 cm^{-1}$	J_{max}
$C^{12}O^{16}_2$	$01^{1c}0-00^00$	667.379 ± .005 (a)	42.5 ± 0.7	0.3 ± 0.1	61.0	68
"	$01^{1d}0-00^00$		103.5 ± 1.0	0.2 ± 0.1		60
"	$02^00-01^{1c}0$	618.033 ± .005 (a)	- 15.9 ± 0.7	2.3 ± 1.0		40
"	$10^00-01^{1c}0$	720.808 ± .005 (a)	- 43.4 ± 0.7	-1.0 ± 1.0		45
"	$02^{2c}0-01^{1c}0$	667.750 ± .005 (a)	102.2 ± 1.2 (d)	0.1 ± 0.8		57
"	$02^{2d}0-01^{1d}0$		41.2 ± 0.7	0.0 ± 0.1		56
"	$03^{1c}0-02^{2c}0$	597.337 ± .008 (a)	- 90.1 ± 1.0		91.9	26
"	$03^{1d}0-02^{2d}0$		1.8 ± 1.0			21
"	$11^{1c}0-02^{2c}0$	741.730 ± .008 (a)	-128.5 ± 1.0		96.4	24
"	$11^{1d}0-02^{2d}0$		- 32.1 ± 1.0			19
"	02^01-00^00	3612.844 ± .004	-271.5 ± 0.7	2.5 ± 0.2		52
"	10^01-00^00	3714.782 ± .002	-315.5 ± 0.3	-1.93 ± .08		64
"	$03^{1c}1-01^{1c}0$	3580.327 ± .003	-285.8 ± 0.7	1.3 ± 0.3	91.5	53
"	$03^{1d}1-01^{1d}0$		-255.3 ± 0.7	1.8 ± 0.3		50
"	$11^{1c}1-01^{1c}0$	3723.250 ± .003	-327.4 ± 0.7	-1.1 ± 0.5	85.9	51
"	$11^{1d}1-01^{1d}0$		-302.5 ± 0.7	-1.8 ± 0.3		58
"	04^21-02^20	3552.872 ± .010	-273 ± 2			27
$C^{12}O^{16}_2$	$12^{2c}1-02^{2c}0$	3726.647 ± .005	-313.9 ± 0.7	-0.8 ± 1.0		34
"	$12^{2d}1-02^{2d}0$		-313.5 ± 0.7	-0.8 ± 0.6		47
"	20^01-10^00	3711.475 ± .010	-269.4 ± 1.0	-1.8 ± 2.0		38
"	12^01-10^00	3589.646 ± .005	-365.5 ± 0.8			22
"	12^01-02^00	3692.416 ± .005	-394.1 ± 0.7			36
"	04^01-02^00	3568.218 ± .008	-229.7 ± 1.0			30
"	00^01-00^00	2349.16 (b)	-309.0 ± 0.5			
"	00^03-00^00	6972.49 (c)	-922.5 ± 0.5			
$C^{12}O^{16}O^{18}$	02^01-00^00	3675.130 ± .005	-260.9 ± 1.0	-2 ± 2		31
"	10^01-00^00	3571.143 ± .008	-287.8 ± 1.0	+2 ± 2		32
$C^{13}O^{16}_2$	10^01-00^00	3632.917 ± .005	-352.4 ± 0.7	-1.7 ± .3		50

(a) Gordon and McCubbin, Reference (10)

(b) Plyler, Blaine and Tidwell, Reference (15)

(c) Courtoy, Reference (6)

(d) Calculated from other bands. ΔB could not be determined for this band because of blended lines.

TABLE XVIII

VIBRATIONAL CONSTANTS FOR $C^{12}O_2^{16}$

Constants or combinations evaluated from levels without resonance or sums of resonating levels		Constants calculated using $x_{12} - 4x_{22} = -11.70$ cm^{-1}	
Quantity	Value, cm^{-1}	Quantity	Value, cm^{-1}
$\omega_1^0 + 4x_{22}$	1342.33	ω_1^0	1335.97
ω_2^0	667.19	x_{12}	-5.37
ω_3^0	2361.66	x_{22}	1.59
x_{11}	-3.10	g_{22}	-1.40
$x_{12} + 4x_{22}$	.97		
x_{13}	-19.27		
$x_{22} + g_{22}$	.19		
x_{23}	-12.51		
x_{33}	-12.50		

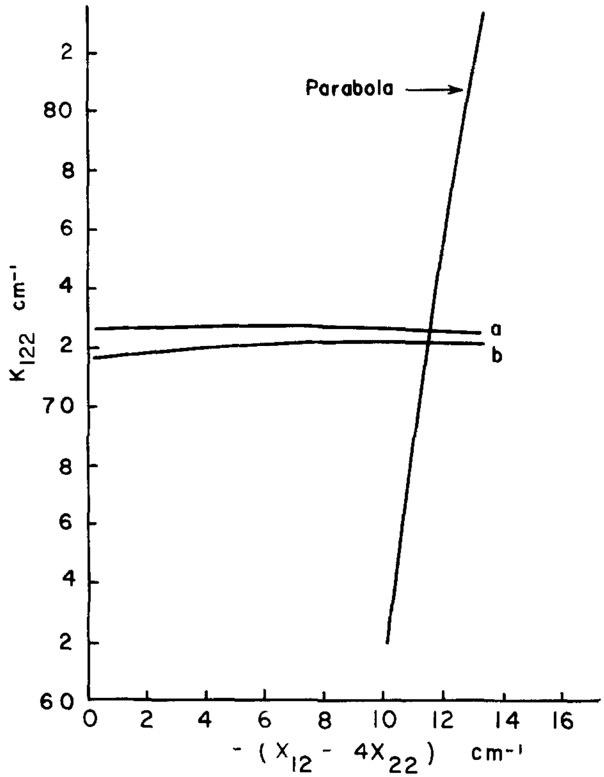

FIG. 1. Plot of $\sqrt{2}w_{12}$ vs $-(x_{12} - 4x_{22})$ for the Σ diads. (a) is the ellipse for the 10^00–02^00 diad and (b) is for the 10^01–02^01 diad.

TABLE XIX

CALCULATED AND OBSERVED FERMI INTERACTION CONSTANTS, cm^{-1}

Diad	$\langle w_{12} \rangle$ (calc)	$\langle w_{12} \rangle$ (obs)
10^00–02^00	58.31	58.31
10^01–02^01	50.95	50.95
11^10–03^10	71.53	71.55
11^11–03^11	71.11	71.13
12^21–04^21	85.98	85.94

TABLE XX

CALCULATED ENERGY LEVELS OF $C^{12}O_2^{16}$

Level	E^0	E(calc)	E(obs)	E(obs) − E(calc)
01^10	667.38	667.38	667.379	0
02^20	1335.14	1335.14	1335.129	−0.01
10^00	1332.87	1388.20	1388.187	−0.01
02^00	1340.74	1285.41	1285.412	0
11^10	1994.88	2076.88	2076.859	−0.02
03^10	2014.48	1932.48	1932.466	−0.01
10^01	3662.76	3714.79	3714.782	−0.01
02^01	3664.88	3612.85	3612.844	−0.01
11^11	4312.26	4390.65	4390.629	−0.02
03^11	4326.11	4247.72	4247.706	−0.01
12^21	4962.14	5061.81	5061.776	−0.03
04^21	4987.72	4888.05	4888.001	−0.05

TABLE XXI

δ CALCULATED FOR EACH DIAD

Diad	$\delta \times 10^5$ cm^{-1}	Weight
10^00–02^00	24.0	2
10^01–02^01	25.0	4
11^10–03^10	25.9	2
11^11–03^11	25.3	4
12^21–04^21	23.7	1
Weighted average value of δ: $25.0 \pm 1.0 \times 10^{-5}$ cm^{-1}		

such a procedure, unless applied to a large number of very accurate vibrational levels, would be physically meaningful.

ROTATIONAL ANALYSIS

In order to evaluate δ in the term $4\langle W_{12}\rangle\delta/\Delta$, Courtoy's values of the vibration–rotation interaction constants α_i and γ_{ij} were used to compute the values of ΔB_0. The results of this calculation are summarized in Table XXI.

TABLE XXII

CALCULATED AND OBSERVED ROTATIONAL CONSTANTS × 10^5

Level	B^0	B(calc)	B(obs)	(Obs − Calc)
00^00	39 021			
01^10	39 093		39 094	+1
02^20	39 164		39 166	+2
10^00	38 902	39 020	39 020	0
02^00	39 168	39 050	39 048	−2
11^10	38 968	39 089	39 086	−3
03^10	39 244	39 122	39 122	0
10^01	38 594	38 703	38 706	+3
02^01	38 858	38 748	38 750	+2
11^11	38 659	38 774	38 779	+5
03^11	38 933	38 818	38 823	+5
12^21	38 725	38 853	38 850	−3
04^21	39 009	38 881	38 893	+12

The observed and calculated B values are given in Table XXII. The disagreement for the 04^21 level probably is the result of experimental error. The other causes of disagreement probably are the inaccuracies in the α_i's and γ_{ij}'s and the neglect of Coriolis resonance. Coriolis resonance cannot be treated because of incomplete information about the resonating levels. The ℓ doubling constants cannot be compared with theory because the effect of the constant δ on ℓ doubling is not known at present.

DISCUSSION OF RESULTS

In this study the method of calculation suggested by Amat and Pimbert has been applied to data most of which have been obtained using the very precise echelle method of wavelength measurement. The third-order y_{ijk} constants have been ignored for reasons mentioned above. Observable energy levels are in close agreement with calculated ones, and the unperturbed 1, v_2^ℓ, v_3 levels of 5 diads fall below the unperturbed 0, $(v_2 + 2)^\ell$, v_3 levels. It therefore should be concluded that the traditional labeling of these almost completely mixed states should be changed.

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