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General Anharmonic Force Constants of Carbon Disulfide

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Twelve force constants in the general quartic force field of carbon disulfide have been determined by a least-squares method from the available spectroscopic data on four isotopic species of carbon disulfide: $^{12}C^{32}S_2$, $^{13}C^{32}S_2$, $^{12}C^{32}S^{34}S$, and $^{13}C^{32}S^{34}S$. A reasonable set of force constants is obtained together with a set of the third-order parameters λ_1, λ_2, λ_3, and δ which appear in Fermi coupling off-diagonal matrix elements. From the converged set of force constants, *l*-type doubling constants for a few π-vibrational states are calculated through a direct numerical diagonalization method of vibrational Hamiltonian matrix. They agree well with the observed *l*-type doubling constants.

In a process of extending the numerical diagonalization technique of vibrational Hamiltonian matrix[1] to the anharmonic treatment of linear symmetric triatomic molecules, it was required to obtain the most reliable set of force constants of CS_2 up to the fourth order. The general quartic force field of CS_2 has previously been studied by Smith and Overend[2] and by Giguere, Wang, Overend, and Cabana.[3] More recently, however, two high resolution infrared studies have been reported on this molecule by Maki[4] and by Blanquet and Courtoy.[5] The study of Maki covers a number of 'hot transitions' in $^{12}C^{32}S_2$ and gives the information of levels which are not directly accessible from the ground state. The study of Blanquet and Courtoy consists of the high resolution measurements of a number of $^{13}C^{32}S_2$ bands. Both studies provide very important pieces of information on the determination of anharmonic force constants of CS_2. Like CO_2, CS_2 is one of a few fundamental molecules, on which the validity of various model potential functions is tested:[6] One of the criteria for this test is whether they can reproduce the values of force constants in the general quartic force field reasonably well or not. It is, therefore, desirable to determine these force constants as precisely as possible. We have carried out such new anharmonic calculations: twelve force constants in the general quartic force field and four third-order parameters, which appear in Fermi coupling off-diagonal matrix elements of $\nu_1=2\nu_2$ type, are adjusted simultaneously to fit the presently available spectroscopic data of $^{12}C^{32}S_2$,[3,4,7–10] $^{13}C^{32}S_2$,[5] $^{12}C^{32}S^{34}S$,[11–13] and $^{13}C^{32}S^{34}S$.[11] The *l*-type doubling constants of $^{12}C^{32}S_2$ and $^{13}C^{32}S_2$ are also obtained from the π-π transitions.[4,5] From the refined set of force constants, the corresponding *l*-type doubling constants are calculated which can be compared with experimental values quite well.

Determination of Anharmonic Force Constants

A general method for the determination of force constants in the general quartic force field was described in the preceding papers[14,15] and it is not repeated here. However, our program of anharmonic calculations has been improved so as to handle 'hot transitions' directly. This is particularly useful when the spectroscopic constants associated with a given hot transition ($\nu_0'-\nu_0''$, $B'-B''$) are determined more accurately than those in the lower state (ν_0'', B'').

The potential functions of linear symmetric triatomic molecules may be expanded in terms of curvilinear internal coordinates through quartic terms and

$$\begin{aligned} V = {} & K_{11}(R_1^2+R_3^2) + K_{13}R_1R_3 + K_{22}R_2^2 \\ & + K_{111}(R_1^3+R_3^3) + K_{122}(R_1+R_3)R_2^2 \\ & + K_{113}(R_1+R_3)R_1R_3 + K_{1111}(R_1^4+R_3^4) \\ & + K_{1113}(R_1^2+R_3^2)R_1R_3 + K_{1133}R_1^2R_3^2 \\ & + [K_{1122}(R_1^2+R_3^2) + K_{1223}R_1R_3 + K_{2222}R_2^2]R_2^2, \end{aligned} \tag{1}$$

where R_1 and R_3 are two stretching coordinates and R_2 is the bending coordinate.[16]

Fermi Resonance in CS_2. The vibrational levels of most non-hydride linear triatomic molecules are more or less affected by Fermi resonance through non-vanishing matrix elements $\langle v_1, v_2, l_2, v_3 | v_1-1, v_2+2, l_2, v_3 \rangle$. To the third order of approximation in perturbation treatment, this matrix element is expressed as

$$\begin{aligned} & (1/2)[-k_{122}/\sqrt{2}+\lambda_1 v_1+\lambda_2(v_2+2)+\lambda_3(v_3+1/2) \\ & \qquad +\delta J(J+1)][(v_2+2)^2-l_2^2]^{1/2}v_1^{1/2} \end{aligned} \tag{2}$$

The λ's and δ represent the third order vibrational and rotational effects on the matrix elements,[17] which cannot be ignored in the determination of the general quartic force field of most linear triatomic molecules.[2,3,15,18] The effect of δ on the perturbed rotational constant in each vibrational state is also taken into account. In the present calculation we are able to treat the third-order parameters of the ^{12}C- and ^{13}C-species separately,[19] thus the total number of independent parameters is twenty.

Spectroscopic Data Used in Computations. The spectroscopic data used in the refinement of twelve general quartic force constants and eight third-order parameters are listed in Table 1 along with the corresponding weights. References are also given in the last column in Table 1. The present system for the weighting is based on the fact that the band centers are usually determined within a few thousandths of a wave number and that the errors in the ΔB values are in the order of 10^{-7} cm^{-1}. The spectroscopic data associated with the transitions from the 02^20 level of $^{12}CS_2$ as well as those from the 01^10 level in $^{13}CS_2$ are used directly, since the spectroscopic constants of the lower states are known less accurately. We employed $r_e=1.5562$ Å for the equilibrium bond distance,

Table 1. Observed and calculated vibrational levels (in cm^{-1}) and rotational constants (in 10^{-4} cm^{-1}) for $^{12}C^{32}S_2$, $^{13}C^{32}S_2$, $^{12}C^{32}S^{34}S$, and $^{13}C^{32}S^{34}S$

Level	ν_{obsd}	Wt.	i	ii	(B_v-B)	Wt.	i	ii	Ref.
(a) $^{12}C^{32}S_2$									
$1\ 0^0\ 0$	658.00	1.0	1	7	−1.55	1.0	4	6	a
$0\ 2^0\ 0$	801.85	1.0	7	6	3.69	1.0	$\underline{1}$	$\underline{3}$	b
$2\ 0^0\ 0$	1313.70	1.0	7	11	−3.02	1.0	3	7	a
$1\ 2^0\ 0$	(1446.97)	0.0			(2.59)	0.0			
$0\ 4^0\ 0$	(1619.76)	0.0			(6.81)	0.0			
$0\ 0^0\ 1$	1535.35	1.0	$\underline{7}$	$\underline{7}$	−7.12	1.0	1	1	b
$1\ 0^0\ 1$	2185.49	1.0	$\underline{3}$	1	−8.67	1.0	2	4	c
$0\ 2^0\ 1$	2324.55	1.0	3	1	−3.43	1.0	3	1	b
$2\ 0^0\ 1$	2833.19	1.0	$\underline{4}$	$\underline{2}$	−10.03	1.0	7	11	d
$1\ 2^0\ 1$	2961.76	1.0	3	2	−4.57	1.0	$\underline{2}$	$\underline{2}$	a
$0\ 4^0\ 1$	3129.98	1.0	1	$\underline{2}$	−0.39	1.0	$\underline{1}$	$\underline{3}$	e
$3\ 0^0\ 1$	3478.39	1.0	$\underline{3}$	$\underline{4}$	−11.33	1.0	2	4	e
$2\ 2^0\ 1$	3597.05	1.0	4	13	−5.71	1.0	$\underline{10}$	$\underline{8}$	a, e
$1\ 4^0\ 1$	3757.45	1.0	$\underline{7}$	$\underline{15}$	−1.32	1.0	$\underline{7}$	$\underline{7}$	a
$0\ 6^0\ 1$	(3948.17)	0.0			(2.41)	0.0			
$0\ 0^0\ 3$	4566.81	1.0	$\underline{1}$	0	−21.35	1.0	4	4	b
$1\ 0^0\ 3$	5201.15	1.0	5	7	−22.91	1.0	$\underline{3}$	$\underline{1}$	e
$0\ 2^0\ 3$	(5330.60)	0.0			(−17.79)	0.0			
$0\ 1^1\ 1$	1924.99	1.0	$\underline{4}$	$\underline{6}$	−5.00	0.1	$\underline{2}$	$\underline{2}$	b
$1\ 1^1\ 1$	2567.51	0.1	5	7	−6.15	0.1	$\underline{4}$	$\underline{2}$	d, c
$0\ 3^1\ 1$	2723.36	0.1	4	7	−1.73	0.1	1	$\underline{1}$	a
$2\ 1^1\ 1$	3207.44	0.5	$\underline{4}$	10	(−7.09)	0.0			d
$1\ 3^1\ 1$	3355.18	0.5	2	6	−2.73	0.1	$\underline{8}$	$\underline{8}$	e, f
$0\ 5^1\ 1$	(3535.69)	0.0			(1.14)	0.0			
$0\ 1^1\ 3$	4943.55	0.1	4	4	(−19.25)	0.0			
$0\ 1^1\ 0$	396.09	1.0	3	0	2.11	1.0	$\underline{4}$	$\underline{4}$	b, f
$1\ 1^1\ 0$	1046.58	1.0	8	8	0.98	1.0	$\underline{0}$	2	b
$0\ 3^1\ 0$	1206.98	1.0	8	12	5.39	0.1	$\underline{5}$	$\underline{7}$	b
$0\ 2^2\ 0$	792.52	0.01	$\underline{22}$	$\underline{15}$	(4.29)	0.0			b
$1\ 2^2\ 1$	(2158.20)†	0.0			(−7.94)	0.0			
$0\ 4^2\ 1$	2329.03†	0.1	$\underline{6}$	3	−4.24	0.1	$\underline{3}$	$\underline{4}$	a
$2\ 2^2\ 1$	(2791.59)†	0.0			(−8.61)	0.0			
$1\ 4^2\ 1$	2955.63†	0.1	$\underline{10}$	5	−5.01	0.1	$\underline{8}$	$\underline{7}$	a
$0\ 6^2\ 1$	(3148.05)†	0.0			(−1.50)	0.0			
(b) $^{13}C^{32}S_2$									
$1\ 0^0\ 0$	657.23	1.0	2	5	−1.57	0.01	$\underline{11}$	$\underline{11}$	g
$0\ 2^0\ 0$	(776.46)	0.0			(3.39)	0.0			
$0\ 0^0\ 1$	1485.34	1.0	$\underline{5}$	$\underline{5}$	−6.87	1.0	$\underline{1}$	$\underline{0}$	g
$1\ 0^0\ 1$	2134.87	1.0	$\underline{4}$	$\underline{2}$	−8.26	1.0	2	2	g
$0\ 2^0\ 1$	2250.13	1.0	1	$\underline{0}$	−3.47	1.0	4	5	g
$2\ 0^0\ 1$	2781.61	1.0	2	$\underline{7}$	−9.44	1.0	5	2	g
$1\ 2^0\ 1$	2886.78	1.0	3	1	−4.54	1.0	4	2	g
$0\ 4^0\ 1$	(3031.24)	0.0			−0.74	0.0			
$3\ 0^0\ 1$	3425.29	0.1	10	$\underline{18}$	−10.38	0.0			g
$2\ 2^0\ 1$	(3521.35)	0.0			(−5.66)	0.0			
$1\ 4^0\ 1$	(3658.53)	0.0			(−1.63)	0.0			
$0\ 6^0\ 1$	(3824.70)	0.0			(1.78)	0.0			
$0\ 1^1\ 0$	(383.02)	0.0			1.96	0.01	$\underline{9}$	$\underline{10}$	g
$0\ 1^1\ 1$	1479.63*	1.0	24	25	−6.85	1.0	1	1	g
$1\ 1^1\ 1$	2120.71*	1.0	$\underline{5}$	$\underline{4}$	−7.82	1.0	0	$\underline{3}$	g
$0\ 3^1\ 1$	2253.60*	1.0	$\underline{1}$	6	−3.90	1.0	7	10	g
$2\ 1^1\ 1$	2759.23*	1.0	2	$\underline{2}$	−8.57	1.0	$\underline{1}$	$\underline{10}$	g
$1\ 3^1\ 1$	(2884.87)*	0.0			(−4.86)	0.0			
$0\ 5^1\ 1$	(3041.52)*	0.0			(−1.39)	0.0			
(c) $^{12}C^{32}S^{34}S$									
$1\ 0^0\ 0$	648.37	1.0	$\underline{17}$	$\underline{18}$	(−1.57)	0.0			i
$0\ 2^0\ 0$	(799.57)	0.0			(3.66)	0.0			
$1\ 0^0\ 1$	2172.77	1.0	0	$\underline{2}$	−8.41	1.0	5	5	h
$0\ 2^0\ 1$	(2318.86)	0.0			(−3.28)	0.0			

Table 1. Continued

Level	ν_{obsd}	Wt.	i	ii	(B_v-B)	Wt.	i	ii	Ref.
0 0^0 3	4556.55	1.0	1	0	−20.73	0.2	2	2	j
0 1^1 0	395.13	1.0	$\underline{2}$	$\underline{5}$	(2.09)	0.0			b
⎡1 1^1 0	1036.42	1.0	$\underline{1}$	$\underline{14}$	(0.86)	0.0			i
⎣0 3^1 0	(1203.53)	0.0			(5.38)	0.0			
0 1^1 3	4932.34	1.0	$\underline{5}$	$\underline{6}$	(−18.66)	0.0			j
0 2^2 0	790.72	1.0	$\underline{21}$	$\underline{13}$	(4.17)	0.0			b
(d) $^{13}C^{32}S^{34}S$									
⎡1 0^0 1	2122.18	1.0	4	4	−8.05	1.0	2	2	h
⎣0 2^0 1	(2244.06)	0.0			(−3.33)	0.0			

†Transitions from the 0 2^2 0 level. *Transitions from the 0 1^1 0 level.
Only differences between observed and calculated frequencies (in 10^{-2} cm^{-1}) and rotational constants (in 10^{-6} cm^{-1}) are given. Negative differences are underlined. Numbers in parenthese are calculated values from set (i).
References: a) Ref. 4. b) Ref. 2. c) Ref. 9. d) Ref. 7. e) Ref. 8. f) Ref. 10. g) Ref. 5. h) Ref. 11. i) Ref. 13. j) Ref. 12.

TABLE 2. FORCE CONSTANTS OF CS_2 IN THE GENERAL QUARTIC FORCE FIELD[a,b]

	(i)	(ii)	(iii)	(iv)[d]
K_{11}	3.9383 (16)	3.9356 (13)	3.9337 (17)	8.0089 (26)
K_{13}	0.6441 (33)	0.6388 (28)	0.6360 (34)	1.2570 (54)
K_{22}	0.2846 (2)	0.2848 (2)	0.2849 (1)	0.3928 (2)
K_{111}	−7.478 (29)	−7.478 (31)	−7.441 (14)	−18.948 (31)
K_{113}	−0.842 (93)	−0.869 (97)	−0.793 (43)	−1.886 (85)
K_{122}	−0.369 (7)	−0.365 (7)	−0.367 (4)	−0.612 (3)
K_{1111}	8.697 (190)	8.924 (172)	8.834 (149)	26.144 (157)
K_{1113}	0.643 (466)	1.390 (401)	1.382 (516)	3.329 (205)
K_{1133}	0.479 (636)	1.483 (535)	1.637 (793)	2.382 (312)
K_{1122}	0.111 (85)	0.253 (70)	0.428 (38)	0.852 (107)
K_{1223}	0.461 (185)	0.771 (146)	1.136 (97)	2.594 (221)
K_{2222}	0.044 (4)	0.037 (3)	0.032 (3)	0.035 (4)
λ_1	0.460 (120)	0.276 (100)	0.141 (112)	0.358 (111)
λ_2	0.325 (86)	0.204 (74)	0.043 (49)	0.498 (48)
λ_3	0.037 (181)	0.018 (130)	−0.041 (193)	0.281 (90)
$\delta\times10^4$	0.378 (32)	0.350 (28)	0.592 (23)	1.966 (79)
λ'_1	0.359 (106)			0.653 (111)
λ'_2	0.301 (90)			0.509 (53)
λ'_3	0.042 (174)			0.275 (91)
$\delta'\times10^4$	0.344 (31)			1.883 (77)
S[c]	0.25	0.35		

a) The units of force constants are: mdyn/Å for K_{11} and K_{13}, mdyn·Å/rad^2 for K_{22}, mdyn/Å^2 for K_{111} and K_{113}, mdyn/rad^2 for K_{122}, mdyn/Å^3 for K_{1111}, K_{1113}, and K_{1133}, mdyn/Å rad^2 for K_{1122} and K_{1223}, and mdyn·Å/rad^4 for K_{2222}. The third order parameters λ's and $\delta\times10^4$ are given in cm^{-1}. In order to retain good reproducibility of the calculated values, four or three significant numbers beyond the decimal point are given, even when the corresponding dispersions are considerably larger than that. b) Dispersions, shown in parentheses, apply to the last digits of the quantity. c) The weighted sum of squared deviations for a given set of force constants and the third order parameters. d) The corresponding force constants of CO_2 (Ref. 15).

Results and Discussion

The converged sets of the anharmonic force constants and the third-order parameters are listed in Table 2 with the corresponding previous results on CS_2 and CO_2. In preliminary calculations the differences of the third-order parameters due to isotopic substitutions were neglected, and the converged set for the sixteen parameter problem is given in column (ii). It was found, however, that the fit in frequency and rotational constant is much improved by allowing the third-order parameters vary for the ^{12}C- and ^{13}C-species, and the twenty parameter problem seems to be stable enough to give a good converged set which is listed in the column (i) of Table 2. The harmonic frequencies ω_i, the anharmonicity constants x_{ij}, the vibration-rotation constants α_i, and the cubic and quartic force constants in dimensionless normal coordinates k_{ijk} and k_{ijkl} are calculated for the four isotopic species of CS_2 from the sets (i) and (ii), their values are listed in Table 3.

Values of Force Constants. The force constants of CS_2 thus determined have the features expected for linear triatomic molecules: (1) They show a dis-

Table 3. Harmonic frequencies (ω_i), anharmonicity constants (x_{ij}), vibration-rotation constants (α_i), and force constants in dimensionless normal coordinates (k_{ijk}, k_{iijj}) calculated from the general quartic force field (in cm^{-1})

Set (i)

	$^{12}C^{32}S_2$	$^{13}C^{32}S_2$	$^{12}C^{32}S^{34}S$	$^{13}C^{32}S^{34}S$
ω_1	672.574	672.574	662.564	662.559
ω_2	398.210	358.057	397.285	385.100
ω_3	1558.849	1507.360	1555.251	1503.642
x_{11}	−1.00	−1.00	−0.97	−0.97
x_{12}	−2.49	−2.40	−2.45	−2.36
x_{22}	1.00	0.94	1.00	0.93
x_{13}	−7.66	−7.43	−7.52	−7.29
x_{23}	−6.45	−6.00	−6.43	−5.98
x_{33}	−6.57	−6.13	−6.55	−6.10
$x_{l_2l_2}$	−0.69	−0.64	−0.69	−0.64
$\alpha_1\times10^4$	2.172	2.172	2.077	2.077
$\alpha_2\times10^4$	−2.146	−2.050	−2.087	−1.993
$\alpha_3\times10^4$	7.130	6.861	6.915	6.654
k_{111}	−18.386	−18.386	−17.978†	−17.978††
k_{122}	43.153	41.728	42.729	41.311
k_{133}	−130.295	−125.992	−129.012	−124.728
k_{1111}	0.593	0.593	0.575	0.575
k_{1122}	−5.392	−5.214	−5.299	−5.123
k_{2222}	1.697	1.587	1.689	1.579
k_{1133}	8.736	8.447	8.585	8.300
k_{2233}	−15.264	−14.273	−15.196	−14.204
k_{3333}	3.826	3.578	3.809	3.561

†$k_{113}=-0.531$, $k_{223}=-1.195$, $k_{333}=1.222$

††$k_{113}=-0.567$, $k_{223}=-1.221$, $k_{333}=1.263$

Set (ii)

	$^{12}C^{32}S_2$	$^{13}C^{32}S_2$	$^{12}C^{32}S^{34}S$	$^{13}C^{32}S^{34}S$
ω_1	672.152	672.152	662.149	662.144
ω_2	398.345	385.188	397.420	384.231
ω_3	1558.838	1507.351	1555.241	1503.631
x_{11}	−0.88	−0.88	−0.85	−0.85
x_{12}	−2.16	−2.08	−2.13	−2.05
x_{22}	0.90	0.84	0.90	0.84
x_{13}	−7.63	−7.40	−7.49	−7.26
x_{23}	−6.46	−6.01	−6.44	−5.99
x_{33}	−6.57	−6.13	−6.55	−6.10
$x_{l_2l_2}$	−0.66	−0.61	−0.66	−0.61
$\alpha_1\times10^4$	2.189	2.189	2.093	2.093
$\alpha_2\times10^4$	−2.152	−2.056	−2.093	−1.999
$\alpha_3\times10^4$	7.131	6.862	6.916	6.655
k_{111}	−18.465	−18.465	−18.055†	−18.055††
k_{122}	43.218	41.790	42.792	41.371
k_{133}	−130.185	−125.885	−128.902	−124.622
k_{1111}	0.685	0.685	0.665	0.665
k_{1122}	−5.089	−4.921	−5.001	−4.835
k_{2222}	1.635	1.529	1.628	1.522
k_{1133}	8.803	8.512	8.650	8.363
k_{2233}	−15.283	−14.290	−15.215	−14.222
k_{3333}	3.818	3.570	3.801	3.553

†$k_{113}=-0.526$, $k_{223}=-1.194$, $k_{333}=1.220$

††$k_{113}=-0.562$, $k_{223}=-1.221$, $k_{333}=1.260$

Table 4. Diagonal stretching force constants associated with the CS bond

	CS_2	CS[a]	OCS[b]
K_{ii} (mdyn/Å)	3.9383	4.2445	3.7215
K_{iii} (mdyn/Å^2)	−7.478	−8.256	−6.670
K_{iiii} (mdyn/Å^3)	8.697	8.858	8.192
$-a_1$ (Å^{-1})	1.90	1.95	1.79
a_2 (Å^{-2})	2.21	2.09	2.20
$a_2{}^*$ (Å^{-2})	2.10	2.21	1.87
r_e (Å)	1.5526	1.5344	1.5630

a) Ref. 20. b) Ref. 21.

tinctive positive-negative-positive pattern for the quadratic, cubic and quartic force constants. (2) Off-diagonal force constants are one order of magnitude smaller than the corresponding diagonal force constants. In addition, the overall feature of the potential function is very close to that of CO_2 which is quite reasonable. In Table 4 three diagonal stretching force constants are listed and compared with the corresponding constants of CS[20] and OCS.[21] The ratios $a_1=K_{111}/K_{11}$, $a_2=K_{1111}/K_{11}$, and $a_2{}^*=7a_1{}^2/12$ are also listed in the table. Within the limits of present approximation, the Morse type potential function[22] seems to be a good model for the CS stretching mode, since the relationship $a_2= a_2{}^*$, which holds strictly in the Morse potential function, is nearly realized in this molecule. We may also estimate the dissociation energy of $CS_2 \rightarrow CS+S$ from an assumption that the stretching potential is of Morse type. Then we have $D_e=K_{11}/a_1{}^2=6.8$ eV. As far as we are aware, no experimental data seem available for this process, but the value is close to that of 7.2 eV for diatomic CS.[23]

Although the least-squares dispersions for the third-order parameters λ's are relatively large, it is gratifying that the converged values are very close to those obtained on purely experimental basis. The isotopic ratios seem also reasonable. The values of harmonic frequencies, anharmonicity constants, vibration-rotation constants, and third-order parameters for $^{12}C^{32}S_2$ are collected in Table 5 from different sources: (1) calculated from the set (i) in the present work, (2) obtained by Blanquet and Courtoy[24] who made the direct least-squares fit of the experimental data to the analytical expressions of the energy levels and the rotational constants, (3) calculated from the force constants given in Ref. 3, and (4) obtained by the same authors by applying the Amat-Pimbert method to experimental data.[25] The agreements (or disagreements rather) in their values indicate, in a way, the precisions of the general quartic force constants and of some spectroscopic constants of the CS_2 molecule. As seen in Table 5, the final set of force constants yields the spectroscopic constants which are very close to those obtained experimentally. This seems to guarantee the consistency of the present anharmonic calculation.

Table 5. Spectroscopic constants of $^{12}CS_2$

	PR[a]	BC[b]	GWOC[c]	AP[d]
ω_1	672.574	672.709	671.89	672.42
ω_2	398.210	398.261	398.38	398.39
ω_3	1558.849	1558.710	1558.73	1558.70
x_{11}	−1.00	−1.021	−0.83	−1.05
x_{12}	−2.49	−2.897	−1.75	−1.13
x_{22}	1.00	1.094	0.82	0.66
x_{13}	−7.66	−7.664	−7.59	−7.62
x_{23}	−6.45	−6.446	−6.49	−6.48
x_{33}	−6.57	−6.540	−6.54	−6.54
$x_{l_2 l_2}$	−0.69	−0.775	−0.74	−0.60
$\alpha_1 \times 10^4$	2.172	2.100	2.144	
$\alpha_2 \times 10^4$	−2.146	−2.130	−2.148	
$\alpha_3 \times 10^4$	7.130	7.142	7.130	
λ_1	0.46	0.49	0.141	
λ_2	0.33	0.42	0.043	
λ_3	0.04	0.02	−0.041	
$\delta \times 10^4$	0.378	0.724	0.592	
k_{122}	43.15	42.31	43.16	44.8

a) Calculated from Set (i). b) Obtained experimentally.[24] c) Calculated from Set (iii).[3] d) Obtained by applying the Amat-Pimbert method.[3]

Unperturbed Energy Levels. Fermi resonances in CS_2 are not so strong as those in CO_2. Nevertheless, the effects are seen on most of energy levels. The unperturbed and perturbed energy levels and rotational constants are calculated from the set (i) in Table 2 and are listed in Table 6 for a few typical Fermi polyads. Shifts of 7—20 cm^{-1} are usually observed. It is also seen that Fermi resonances in $^{13}C^{32}S_2$ are stronger than those in $^{12}C^{32}S_2$, as is expected from the lowering of the ν_2 frequency on the ^{13}C-substitution.

l-Type Doubling Constants. From the analyses of the π-π transition bands, the *l*-type doubling constants have been determined for a few vibrational states of $^{12}C^{32}S_2$ and $^{13}C^{32}S_2$.[4,5] The dependence of *l*-type doubling constants on vibrational quantum numbers has previously been explored by Nakagawa and Morino who used the contact transformation method.[26] The *l*-type doubling in linear molecules arises essentially from the Coriolis Hamiltonian term which connects

Table 6. Unperturbed and perturbed energy levels and rotational constants (in cm^{-1})

Level	$E_v{}^0$	E_v	$B_v{}^0 \times 10^4$	$B_v \times 10^4$
(i) $^{12}C^{32}S_2$				
1 0 0	664.27	657.99	1083.91	1084.50
0 2^0 0	795.50	801.78	1090.37	1089.78
1 0 1	2192.03	2185.52	1076.78	1077.40
0 2^0 1	2318.02	2324.52	1083.24	1082.62
2 0 1	2846.64	2833.23	1074.60	1075.98
1 2^0 1	2969.65	2961.73	1081.07	1081.53
0 4^0 1	3108.64	3129.97	1087.53	1085.70
1 1^1 1	2579.15	2567.46	1078.92	1079.97
0 3^1 1	2711.64	2723.32	1085.39	1084.34
(ii) $^{13}C^{32}S_2$				
1 0 0	664.47	657.21	1083.95	1084.66
0 2^0 0	769.19	776.46	1090.22	1089.51
1 0 1	2142.44	2134.91	1077.09	1077.84
0 2^0 1	2242.58	2250.12	1083.36	1082.61
2 0 1	2797.50	2781.59	1074.91	1076.63
1 2^0 1	2894.84	2886.75	1081.18	1081.54
0 4^0 1	3007.25	3031.24	1087.46	1085.38

Table 7. Observed and calculated *l*-type doubling constants (in 10^{-5} cm^{-1})

$^{12}C^{32}S_2$			$^{13}C^{32}S_2$		
Level	q_{obsd} a)	q_{calcd}	Level	q_{obsd} b)	q_{calcd}
0 1^1 0	7.82	7.65	0 1^1 0	8.52	7.92
1 1^1 0	9.05	8.63	0 1^1 1	8.68	7.84
0 3^1 1	14.65	14.31	1 1^1 1	9.75	9.00
1 3^1 1	15.78	14.96	0 3^1 1	15.19	14.53
			2 1^1 1	11.60	10.18

a) Ref. 4. b) Ref. 5.

with the $l=\pm 1$ levels through a common $l=0$ level. The effect of vibrational anharmonicities on *l*-type doubling constants may be evaluated if the perturbed vibratioanl wave functions are known. This is most easily done by solving the vibrational Hamiltonian matrix numerically. The eigenvectors indicate the mixings of the basis harmonic wave functions through the vibrational anharmonicity.1) The *l*-type doubling constant for a given π-state may then be calculated numerically from the perturbed wave functions.27) In Table 7, the *l*-type doubling constants calculated from the converged set (i) are listed and compared with the experimental values. In most cases the calculated constants are slightly smaller than the observed, however, differences are small and they show a remarkably similar trend in their dependence on vibrational quantum numbers as well as on isotopic substitutions.

Concluding Remarks. We believe that the general quartic force constants and the third-order parameters determined in the present work are as good as the corresponding constants in the CO_2 molecule.15) In order to secure their reliability, however, more experimental works should be needed especially on low-lying vibrational levels of the ^{13}C- and ^{34}S-species. The measurements along this line is being planned.

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