SUB-DOPPLER HIGH-RESOLUTION SPECTROSCOPY OF 15V BAND OF CS₂ AND THE ZEEMAN EFFECT

ATSUSHI DOI, MASAYA OHTSUKA, KIYOSHI NISHIZAWA, MASAOKI
BABA* and HAJIME KATÔ

*Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe
657, Japan*

**Present address: Faculty of Integrated Human Studies, Kyoto University, Kyoto
606, Japan*

(Received 13 March, 1994)

Excitation spectra and the Zeeman spectra of CS₂ in the region of 31320–31445 cm⁻¹ were measured with sub-Doppler resolution. Observed rotational lines were classified to 14 series of lines (vibronic bands) and were named by the wavenumbers of their band origins. The 31344.9 band is the strongest one and is assigned as the main band of the $V^1B_2(0v_2,0(K=0)) - X^1\Sigma_g^+(00^0,0)$ transition. Most of the extra bands may be allowed by the vibronic interaction between the $V^1B_2(0v_2,0(K=0))$ level and singlet levels, which are mostly high vibrational levels of the $^1A_1(X^1\Sigma_g^+)$ state. The Zeeman splittings are observed for several lines in almost all bands. These may be originating from the spin-orbit interaction between the rotational levels, which have accidentally nearly the same energy, of the $^1A_1(X^1\Sigma_g^+)$ state and the $^3A_2(^3\Delta_u)$ or/and $^3B_2(^3\Delta_u)$ state.

KEY WORDS: CS₂, Zeeman effect, V band, Sub-Doppler high-resolution spectroscopy.

I. INTRODUCTION

The electronic absorption spectrum of CS₂ in the region 3300–2900 Å is named as the V system by Kleman. [1] The vibrational and rotational structure was first analyzed in detail by Jungen *et al.*, [2] and the V system was assigned as the transition to the bent 1B_2 state which correlates with the $^1\Delta_u[(\pi_g)^3\pi_u]$ state of a linear molecule. [3] The bands of the V system were named 1V, 2V, . . . , and were listed in Table 3 of Ref. 2. Ochi *et al.* [4] observed the fluorescence excitation spectra and the Zeeman quantum beats for the V system of CS₂ cooled in a supersonic jet. The rotational temperature was reduced to less than 10 K and the fluorescence excitation spectrum was simplified. Cramb *et al.* [5] observed picosecond laser-induced quantum beats and rotationally resolved spectra of the 10V and 15V band systems, and identified some of the perturbing levels. By using a single-frequency laser of linewidth less

than 0.0001 cm^{-1} crossed to a molecular beam of CS_2 , Nishizawa *et al.* [6] observed the rotationally resolved excitation spectra and the Zeeman spectra with sub-Doppler resolution for the 6V, 10V and 13V band systems. Many more lines were identified with higher resolution, and the magnetic moments of the upper levels were obtained from the magnitude of the Zeeman splittings. We have extended the observation of the excitation spectra and the Zeeman spectra with sub-Doppler resolution to the 15V band system. The results and the analysis are reported in this article.

II. EXPERIMENTAL

The experimental setup is almost the same with the one in our previous report, [6] and the diagram is shown in Fig. 1. A single-frequency UV light was produced by installing an angle tuned frequency doubler (a LiIO_3 crystal) within the cavity of a ring laser (CR699–29). When the frequency doubler is installed, the machine (CR699–29) loses its autoscanned operation capability. The autoscanned operation in the UV region was made possible by the same method as given in a previous report. [7] The laser power was about 1 mW and the linewidth was about 2 MHz. The frequency of the laser light was calibrated by using the fundamental light; the excitation spectrum of I_2 and frequency marks of an etalon with 150 MHz free spectral range were recorded simultaneously. Some parts of the excitation spectrum and the Zeeman spectrum are shown in Figs. 2 and 3. We measured the excitation spectrum

Figure 1 Experimental diagram of sub-Doppler excitation spectroscopy and the Zeeman spectroscopy.

Figure 2 A part of the fluorescence excitation spectrum and the Zeeman spectrum at $H = 210$ G around the P branches of the 31344.9 band. Lines without a notation are mostly those of $J' \geq 12$. Expanded Zeeman spectra of $P(8)$ lines are shown above the corresponding lines.

Figure 3 A part of fluorescence excitation spectrum and the Zeeman spectrum at $H = 210$ G around the R branches of the 31344.9 band. Lines without a notation are mostly those of $J' \geq 12$. Expanded Zeeman spectra of $R(6)$ lines are shown above the corresponding lines.

of a spectral range of 1 cm^{-1} in a single scan, and then the Zeeman spectrum in the same energy region was measured by applying the magnetic field without changing the optical arrangement. By this procedure, we measured the spectra in a chosen energy region. The direction of an electric vector of laser light was perpendicular to the magnetic field. The linewidth (FWHM) of an unperturbed line was about 20 MHz, which was due to the residual Doppler width.

III. RESULTS AND DISCUSSION

CS_2 is linear in the ground state $X^1\Sigma_g^+(\pi_g)^4$. [3] Let us express a vibrational angular momentum quantum number about the top axis originating from the degenerate bending vibration ν_2 by l ; $l = \nu_2, \nu_2-2, \nu_2-4, \dots, 1$ or 0 , where ν_2 is the vibrational quantum number. We shall use the notations J , K , and M to specify the quantum numbers of, respectively, the total angular momentum $\mathbf{J}$ of a rotational level, the projection of the rotational angular momentum $\mathbf{N}$ along the molecule-fixed top axis, and the projection of $\mathbf{J}$ along the space-fixed Z axis. $K = l$ in the $X^1\Sigma_g^+$ state. Because of the zero nuclear spin of the ^{32}S nuclei in $^{12}\text{C}^{32}\text{S}_2$, only even J'' levels are allowed for $l = 0$ by the nuclear spin statistics. [8] Hence, absorption lines only from even J'' levels are observed for $\nu_2'' = 0$.

The spectral lines whose band head positions are at $31339\text{--}31360$ and 31424 cm^{-1} are classified as $15V$ band system. [2] We measured the excitation spectra and the Zeeman spectra in the region of $31320\text{--}31445\text{ cm}^{-1}$. By using the molecular constants of the ground state [9] and by referring the line intensities, we first searched for the P and R branch lines having a common upper rotational level from the combination difference. [8] The Zeeman splitting of the $X^1\Sigma_g^+$ state is small and can be neglected. Hence the Zeeman splitting of a spectral line is attributed to the one of the excited level. The Zeeman spectra are useful to confirm the assignments, because the Zeeman splittings of lines of a common upper level should be of the same magnitude, *i.e.* the splittings of $P(J' + 1)$, $Q(J')$, and $R(J' - 1)$ lines should be the same.

We identified 14 series of lines (14 vibronic bands) in this region, and we named these bands by the wavenumbers of the band origins. The line energies and the line intensities are listed in Table I. The accuracy of the intensity is low (about $\pm 20\%$). The Fortrat diagrams are shown in Fig. 4. All the bands except the 31392.3 band are composed of only the P and R branches of even J'' and are identified as the transitions from the $X^1\Sigma_g^+ 00^0 0$ level by the spacing between the $P(J' + 1)$ and $R(J' - 1)$ lines. These bands are assigned as $\Sigma(K = 0) - \Sigma(l = 0)$ transitions. The 31392.3 band is composed of the P , Q , and R lines of even and odd J'' and is identified as the transition from the $X^1\Sigma_g^+ 01^0 0$ level by the spacing between the $P(J' + 1)$, $Q(J')$, and $R(J' - 1)$ lines. The intensities of Q lines are smaller than those of the P and R lines. Hence, this band is assigned as a $\Pi(K = 1) - \Pi(l = 1)$ transition. All the observed bands are found to be transitions of $\Delta K = 0$, *i.e.* the transition moments are along the top axis (*parallel band*). [8]

Figure 4 Fortrat diagrams for the 15V band system. The extrapolated curves (solid lines) are calculated from the molecular constants listed in Table II.

The grouping of rotational lines to each band is simple and unique, but multiple lines are assigned for a given J' in several bands. The multiple lines can appear by intensity borrowing induced by perturbation between the levels close in energy. When only two lines were observed for a given J' in a band, the deperturbed term energies were calculated by the same way as our previous report. [6] When more than two lines were observed for a given J' , the deperturbed term energy $E_o(v', J')$ was approximated by the center of gravity;

$$E_o(v', J') = \sum_i [I_i(v', J' - v'', J'') E_i(v', J')] / \sum_i I_i(v', J' - v'', J''), \quad (1)$$

where $I_i(v', J' - v'', J'')$ is the line intensity of the $V_i(v', J') - X^1\Sigma_g^+(v'', J'')$ transition and $E_i(v', J')$ is the term energy of an excited level $V_i(v', J')$. The term energy is a sum of the line energy and the energy of the $X^1\Sigma_g^+(v'', J'')$ level, which is calculated from the molecular constants in Ref. 9. The resulting term energies are listed in Table

II. By expressing the term energy of the excited level approximately as $G_v + B_v[J(J + 1) - K^2]$, we calculated the values of G_v and B_v for each band by a least-squares fitting to the term energies. The results are listed in Table II.

The Zeeman energy of a JM level is expressed by [10]

$$E_Z(JM) = -g_J \mu_B M H, \quad (2)$$

where g_J is a g -factor of a JM level, μ_B is the Bohr magneton, and the magnetic field H is along the Z axis. The g_J values greater than 0.01 are listed in Table I. The magnetic moment μ_J of a J level can be evaluated by $[J(J + 1)]^{1/2} g_J$ in units of μ_B , and the values are listed in Table I.

Table I Assigned rotational lines in the 15V band system. Transition energies of $P(J' + 1)$, $Q(J')$, and $R(J' - 1)$ lines are in units of cm^{-1} . I is the relative line intensity. g_J and μ_J are, respectively, g -factor and the magnetic moment (in units of Bohr magneton) of upper level.

J'	$P(J' + 1)$	I	g_J	$Q(J')$	I	g_J	$R(J' - 1)$	I	g_J	μ_J
31325.3 band										
1	31324.8317	94					31325.4858	61		
3	31324.4970	118	0.02				31326.0283	101	0.02	0.07
5	31324.1310	85					31326.5307	35		
7	31323.8547	85	0.02				31327.1292	37	0.02	0.13
9	31323.6332	67					31327.7819	46		
31329.9 band										
1	31329.4523	36					31330.1037	37		
3	31329.1598	42					31330.6814	68		
5	31328.8713	29					31331.2737	60		
31340.5 band										
1	31340.1399	8	0.51				31340.7938	7	0.51	0.72
3	31339.6330	28	0.06				31341.1645	25	0.07	0.23
5	31339.3067	49	0.05				31341.7096	60	0.05	0.27
7	31339.0092	66	0.03				31342.2847	48	0.03	0.22
9	31338.7374	58	0.02				31342.8834	57	0.02	0.19
11	31338.5127	24	0.02				31343.5313	24	0.02	0.23
31344.9 band										
1	31344.4968	196					31345.1511	151		
1	31344.5962	25					31345.2481	16		
3	31344.2462	413					31345.7723	275		
3	31344.3095	20					31345.8355	17		
5	31343.1988	89					31345.5988	93		
5	31343.5245	148					31345.9246	140		
5	31344.0394	281					31346.4396	329		
7	31342.9082	116	0.07				31346.1829	108	0.07	0.52
7	31343.5830	318	0.01				31346.8531	212	0.01	0.07
7	31344.0884	42					31347.3621	37		
9	31342.5184	141					31346.6664	180		
9	31343.3103	67					31347.4591	53		
9	31343.9875	58	0.01				31348.1378	73	0.01	0.09
11	31342.1818	89	0.01				31347.2014	123	0.01	0.11
31380.4 band										
1	31379.8539	19					31380.5123	14		
3	31379.4850	23					31381.0155	21		
5	31379.0241	41	0.02				31381.4258	45	0.02	0.11
7	31378.7730	47	0.02				31382.0460	54	0.02	0.15
9	31378.5521	19	0.01				31382.6939	25	0.02	0.14

Table I (Cont'd)

J'	$P(J' + 1)$	I	g_J	$Q(J')$	I	g_J	$R(J' - 1)$	I	g_J	μ_J
11	31377.5831	13					31382.5987	31		
				31389.6 band						
5	31388.2615	22					31390.6632	25		
5	31388.3542	67					31390.7557	74		
7	31387.9828	46	0.01				31391.2630	56	0.01	0.07
9	31387.3275	128					31391.4782	105		
9	31387.6318	23					31391.7811	15		
11	31386.9189	36					31391.9371	30		
11	31386.9361	32					31391.9542	37		
11	31386.9734	20					31391.9915	26		
13	31386.3820	58					31392.2770	70		
13	31386.5338	51					31392.4282	58		
15	31386.1836	71					31392.9507	71		
17	31385.7555	67	0.01				31393.3976	85	0.01	0.17
19	31385.4142	29					31393.9308	33		
19	31385.4421	15					31393.9583	28		
21	31384.9268	40	0.01				31394.3068	47	0.01	0.21
23	31384.4766	43					31394.7264	55		
23	31384.5294	20					31394.7828	37		
25	31384.2628	23	0.01				31395.3878	32	0.01	0.25
				31388.9 band						
1	31388.4243	43					31389.0754	30		
3	31387.9739	51	0.02				31389.5085	48	0.03	0.09
5	31387.5619	79	0.02				31389.9651	61	0.02	0.11
7	31387.2272	28	0.01				31390.4982	19	0.01	0.07
7	31387.3400	25	0.03				31390.6137	27	0.03	0.22
7	31387.4139	35	0.02				31390.6872	32	0.02	0.15
9	31386.5953	26					31390.7426	22		
9	31386.6406	65					31390.7876	60		
				31390.9 band						
1	31390.6073	24					31391.2658	12		
3	31390.0250	60					31391.5525	59		
5	31389.6740	60					31392.0715	89		
7	31389.1263	87	0.01				31392.4047	95	0.02	0.11
9	31388.8886	150	0.02				31393.0396	140	0.01	0.14
11	31388.3996	32					31393.4203	42		
11	31388.6773	36					31393.7011	44		
13	31388.0574	57					31393.9529	58		
17	31387.7365	34					31395.3725	52		
				31392.3 band						
1	31391.8725	55	0.03	31392.3114	51	0.03				0.04
2	31391.7348	57		31392.3868	18		31392.8252	39		
2	31391.8046	18		31392.4564	7		31392.8929	13		
3	31391.6813	113		31392.5547	16		31393.2088	84		
4	31391.5748	137		31392.6636	13		31393.5397	146		
5	31391.4597	62		31392.7727	5		31393.8627	35		
6	31391.3621	71	0.02	31392.8946	10		31394.2000	85	0.02	0.13
7	31391.2601	15					31394.5358	16		
8	31391.1800	55	0.02				31394.8900	57	0.02	0.17
10	31391.0493	17					31395.6388	26		
				31410.9 band						
1	31410.3681	43					31411.0218	45		
3	31410.0072	57					31411.5378	60		
5	31409.4947	69					31411.8950	71		

Table I (Cont'd)

J'	$P(J' + 1)$	I	$g_{J'}$	$Q(J')$	I	$g_{J'}$	$R(J' - 1)$	I	$g_{J'}$	$\mu_{J'}$
7	31409.1099	37					31412.3886	25		
7	31409.0029	22	0.01				31412.2754	24	0.01	0.07
7	31409.1515	21					31412.4186	33		
9	31408.6113	48					31412.7609	53		
11	31407.7547	49					31412.7700	49		
11	31408.5914	27					31413.6126	39		
15	31406.8666	24					31413.6352	22		
15	31407.0580	22					31413.8176	24		
				31420.2 band						
1	31419.6983	116	0.05				31420.3545	61	0.05	0.07
3	31419.3787	179					31420.9083	139		
5	31418.8299	65	0.04				31421.2361	29	0.04	0.22
5	31419.0294	211					31421.4313	142		
7	31418.5890	85					31421.8649	186		
9	31417.3896	81	0.01				31421.5344	73	0.01	0.09
9	31418.2853	32	0.01				31422.4359	80	0.01	0.09
11	31417.4611	171					31422.4840	198		
13	31416.9963	44					31422.8924	58		
13	31417.0386	53					31422.9347	63		
15	31416.3093	42					31423.0810	62		
15	31416.4899	28					31423.2601	31		
17	31416.0766	26					31423.7219	33		
				31422.2 band						
1	31421.8665	31					31422.5245	24		
3	31421.3078	40	0.02				31422.8405	39	0.02	0.07
5	31421.0660	36	0.03				31423.4698	58	0.03	0.16
7	31420.6700	28	0.03				31423.9488	34	0.03	0.22
7	31420.8605	49	0.05				31424.1351	44	0.05	0.37
9	31420.3687	30					31424.5186	43		
9	31420.5322	57	0.03				31424.6787	80	0.03	0.28
11	31420.0774	58					31425.0969	105		
				31427.3 band						
1	31426.8380	47					31427.4869	34		
3	31426.3225	19					31427.8551	21		
3	31426.5621	52					31428.0770	77		
5	31426.4022	21	0.01				31428.7985	35	0.02	0.08
7	31425.4493	89	0.02				31428.7233	108	0.02	0.15
7	31425.7956	24	0.02				31429.0677	34	0.02	0.15
9	31425.4089	45	0.01				31429.5576	60	0.01	0.09
11	31424.4922	15					31429.5112	16		
11	31425.1986	46	0.01				31430.2178	53	0.01	0.11
13	31424.5402	24					31430.4292	28		
				31440.3 band						
1	31439.9178	17	0.11				31440.5788	12	0.12	0.16
3	31439.3425	25	0.03				31440.8733	17	0.04	0.12
5	31439.0229	25	0.01				31441.4286	15	0.01	0.05
7	31438.4132	30	0.01				31441.6865	28	0.01	0.07
9	31438.0629	38					31442.2112	38		
11	31437.7330	34					31442.7515	35		
13	31437.2847	19	0.02				31443.1781	19	0.02	0.27

Table II Term energy of upper level and the Molecular constants G_v and B_v in units of cm^{-1} .

J'	Term energy	G_v and B_v	J'	Term energy	G_v and B_v
		31325.3 band			31392.3 band
1	31325.4861	$G_v = 31325.2709(142)$	1	31788.5172	$G_v = 31788.3945(361)$
3	31326.6813	$B_v = 0.1151(3)$	2	31789.0499	$B_v = 0.1194(7)$
5	31328.7137		3	31789.8546	
7	31331.7120		4	31790.8398	
9	31335.6378		5	31792.0397	
		31329.9 band	6	31793.4711	
1	31330.1054	$G_v = 31329.8822(280)$	7	31795.1205	
3	31331.3392	$B_v = 0.1194(15)$	8	31797.0013	
5	31333.4554		10	31801.4636	
		31340.5 band			31410.9 band
1	31340.7942	$G_v = 31340.4998(273)$	1	31411.0223	$G_v = 31410.8829(303)$
3	31341.8174	$B_v = 0.1138(4)$	3	31412.1911	$B_v = 0.1075(3)$
5	31343.8910		5	31414.0777	
7	31346.8670		7	31416.9495	
9	31350.7407		9	31420.6164	
11	31355.5354		11	31425.1110	
		31344.9 band	15	31436.6426	
1	31345.1616	$G_v = 31344.9096(1170)$			31420.2 band
3	31346.4312	$B_v = 0.1154(17)$	1	31420.3538	$G_v = 31420.2312(640)$
5	31348.3429		3	31421.5621	$B_v = 0.1081(4)$
7	31351.3032		5	31423.5732	
9	31355.0267		7	31426.4470	
11	31360.3437		9	31429.7548	
		31380.4 band	11	31434.4859	
1	31380.5105	$G_v = 31380.3824(1340)$	13	31439.9363	
3	31381.6689	$B_v = 0.1096(19)$	15	31446.0594	
5	31383.6078		17	31453.3994	
7	31386.6296				31422.2 band
9	31390.5533		1	31422.5229	$G_v = 31422.2539(519)$
11	31394.6043		3	31423.4928	$B_v = 0.1129(7)$
		31389.6 band	5	31425.6508	
5	31392.9147	$G_v = 31389.5696(452)$	7	31428.6426	
7	31395.8430	$B_v = 0.1095(1)$	9	31432.4795	
9	31399.3753		11	31437.1005	
11	31403.9617				31427.3 band
13	31409.3686		1	31427.4898	$G_v = 31427.3879(988)$
15	31415.8655		3	31428.6824	$B_v = 0.1106(10)$
17	31423.0767		5	31430.9832	
19	31431.2583		7	31433.3844	
21	31440.1389		9	31437.4135	
23	31449.9635		11	31442.0528	
25	31460.8604		13	31447.4541	
		31388.9 band			31440.3 band
1	31386.0772	$G_v = 31388.8829(862)$	1	31440.5757	$G_v = 31440.2641(484)$
3	31390.1598	$B_v = 0.1085(17)$	3	31441.5265	$B_v = 0.1094(5)$
5	31392.1464		5	31443.6086	
			7	31446.2699	

Table II (Cont'd)

J'	Term energy	G_v and B_v	J'	Term energy	G_v and B_v
7	31395.1947		9	31450.0673	
9	31398.6319		11	31454.7556	
			13	31460.2008	
		31390.9 band			
1	31391.2639	$G_v = 31390.8833(605)$			
3	31392.2074	$B_v = 0.1113(4)$			
5	31394.2556				
7	31396.9856				
9	31400.8944				
11	31405.5687				
13	31410.9745				
17	31425.0546				

The 31344.9 band is the strongest one in the 15V band system. Two or three lines with small random spacings are observed for each J' . The line intensity of an allowed $(v', J') - (v'', J' + 1)$ transition at a temperature T is proportional to [8]

$$C(J' + 1) \exp[-B_v(J' + 1)(J' + 2)hc/kT], \quad (3)$$

where C is a constant proportional to a square of the transition moment and k is the Boltzmann's constant. The sum of the line intensities of the multiple lines for a given J' is shown by a full bar in Fig. 5. The dependence of J' is similar to the one of an allowed transition (open bars in Fig. 5). Therefore, the lines of minor intensity for each J' may be allowed through the intensity borrowing, which is induced by the perturbation with nearby levels (the selection rule is $\Delta J = 0$). [8] The Zeeman splittings are observed to be small except $P(8)$ and $R(6)$ lines. Therefore, the 31344.9 band is confirmed as a transition to a singlet state. The lines of major intensity for each J' in the 31344.9 band are assigned as the $V^1B_2 0v_2 0(K=0) - X^1\Sigma_g^+ 00^0 0$ transition. Although the vibrational assignments are not conclusive, [4] Jungen *et al.* [2] assigned $v_2 = 1$ for the 15V band.

As we can see in Figs. 2 and 3, the magnitudes of Zeeman splittings of the $P(8)$ line at 31342.9082 cm^{-1} and the $R(6)$ line at 31346.1829 cm^{-1} are the same. In the same way, the ones of the $P(8)$ line at 31343.5830 cm^{-1} and the $R(6)$ line at 31346.8531 cm^{-1} are the same. The formers are weaker in the line intensity and larger in the Zeeman splitting than the latters. The upper level of the latters is therefore assigned to $V^1B_2 0v_2 0(K=0, J'=7)$. The upper level of the formers is assigned to a triplet state, to which transition is allowed by the spin-orbit interaction with the $V^1B_2 0v_2 0(K=0, J'=7)$ level. The other extra lines of the 31344.9 band can be identified as transitions to rovibronic levels of a singlet state. The perturbations are observed to increase with J . Hence most of the extra lines may be allowed by the Coriolis interaction between the $V^1B_2 0v_2 0(K=0)$ level and a variety of rovibronic levels of the $^1A_2(^1\Sigma_u^-)$ and/or $^1A_1(X^1\Sigma_g^+)$ states, which are accidentally close in energy with the $V^1B_2 0v_2 0(K=0)$ level.

Figure 5 Sum of the observed intensities of the multiple $P(J' + 1)$ lines for a given J' of the 31344.9 band is shown by a filled bar. The line intensities of allowed $(v', J') \rightarrow (v'', J' + 1)$ transitions at 15 K are calculated from Eq. (3), and are shown by open bars, where the constant C is fitted to the observed one of the $P(6)$ line.

Pique *et al.* [11] observed the dispersed fluorescence spectrum to the $X^1\Sigma_g^+$ ground state by exciting the 15V $R(4)$ line at 31346.45 cm^{-1} . They identified the fluorescence lines to $v_3'' \neq 0$, and interpreted as it is originating from the Coriolis interaction between the excited vibronic levels $V^1B_2 a_1(K = 0)$ and $V^1B_2 b_2(K = 1)$. Coriolis interaction can take place only between levels of the same J . [8] Pique *et al.* used a laser of linewidth of 2 GHz. As we can see in Fig. 3, a few unassigned lines are observed within 2 GHz from the $R(4)$ line at $31346.4396 \text{ cm}^{-1}$. But those are not lines of $J' = 5$, because the corresponding $P(6)$ lines are not observed around the $P(6)$ line at $31344.0394 \text{ cm}^{-1}$ (see Fig. 2). We found two extra $R(4)$ lines at 31345.5988 and $31345.9246 \text{ cm}^{-1}$. If the dispersed fluorescence spectra with exciting the extra lines were observed, we would be able to confirm the interpretation by Pique *et al.* [11]

In the 31340.5 band, appreciable Zeeman splittings are observed for all the assigned lines. Hence, the band may be assigned to the transition to the triplet state $^3A_2(^3\Delta_u)$, which is allowed by the spin-orbit interaction with the $V^1B_2 0v_20(K = 0)$ level. In the other extra bands, the Zeeman splittings are observed to be small, and appreciable Zeeman splittings are observed only for several lines. Hence, most of

the excited states may be identified as singlet states. The Renner-Teller interaction can be neglected in the levels of $K = 0$. [8] Because the quantum number v_2 of the 31344.9 band is expected to be small, the number of levels which can interact by the Fermi resonance within the V^1B_2 state is estimated to be small. Most of the extra bands may be allowed by the vibronic interaction between the $V^1B_2 0v_2 0$ ($K = 0$) level and singlet states. CS_2 has normal vibrations of the symmetry $A_1(v_1 \text{ and } v_2)$ and $B_2(v_3)$. Therefore, only 1B_2 and 1A_1 states can mix with the V^1B_2 state by the vibronic interaction. A number of extra bands can be allowed only by interactions with a state of high level density. The dissociation limit of the $^1A_1(X^1\Sigma_g^+)$ state is estimated to be $35970 \pm 130 \text{ cm}^{-1}$. [11] Therefore, most of the extra bands may be allowed by the vibronic interaction between the $V^1B_2 0v_2 0$ ($K = 0$) level and a high vibrational level of the $^1A_1(X^1\Sigma_g^+)$ state. The 31392.3 band, which is observed to be a transition from the $X^1\Sigma_g^+ 01^0$ level, may be allowed by the vibronic interaction between the $V^1B_2 0v_2 0$ ($K = 1$) level and a high vibrational level of the $^1A_1(X^1\Sigma_g^+)$ state.

It should be noted that the Zeeman splittings are observed for several lines in almost all bands. This may be originating from the spin-orbit interaction between a triplet state and a high vibrational level of the $^1A_1(X^1\Sigma_g^+)$ state. If the spin-orbit interaction between a triplet state and the $V^1B_2 0v_2 0$ ($K = 0$) level is responsible for the Zeeman splitting, the Zeeman splittings should be observed for all the lines of the same J , but the observed results are different. Symmetry allowed perturbing triplet states are 3A_2 , 3B_1 , and 3B_2 . Among the states which arise from the configuration $(\pi_g)^3\pi_u$, [3] $^3A_2(^3\Sigma_u^-)$, $^3A_2(^3\Delta_u)$, $^3B_2(^3\Delta_u)$, and $^3B_2(^3\Sigma_u^+)$ states can be candidates of the perturbing states. The level of the perturbing triplet state must be close in energy to the high vibrational level of the $^1A_1(X^1\Sigma_g^+)$ state, and the level density must be high because the Zeeman splittings are observed for several lines in almost all bands. Hence, the most probable perturbing triplet state is the $^3A_2(^3\Delta_u)$ or/and $^3B_2(^3\Delta_u)$ state.

The V system is strongly perturbed. Merer *et al.* [12] classified the long wavelength part as “*shattered band*” and the short wavelength part as “*quantum chaos*”. By observing the excitation spectra and the Zeeman spectra with sub-Doppler resolution, 14 vibronic bands are classified in the energy range of the 15V band system. The 31344.9 band, which is the strongest band of the 15V band system, is found to be perturbed by nearby levels, and the deperturbation analysis is performed. The magnetic character of the excited states are made clear and the origins of the extra bands are estimated. However, the deperturbation analysis of the vibrational levels is not yet performed, and even the assignment of the vibrational quantum number of the main band is not yet conclusive. We do hope that we would be able to understand this complicated band system by extending these high-resolution spectroscopy to whole bands of the V system.

IV. ACKNOWLEDGMENTS

The authors are very grateful to Dr. K. Ishikawa, J. Nagayama, and S. Kubo for their help, and Dr. J. T. Hougen for valuable discussions. K. N. thanks to JSPS Fellowships for Japanese Junior Scientists. H. K. thanks to the Ministry of Education, Science and Culture of Japan for a Grant-in-Aid for Specially Promoted Research.

References

1. B. Klemm, Can. J. Phys. **41**, 2034 (1963).
2. Ch. Jungen, D. N. Malm and A. J. Merer, Can. J. Phys. **51**, 1471 (1973).
3. R. S. Mulliken, Can. J. Chem. **36**, 10 (1958).
4. N. Ochi, H. Watanabe, S. Tsuchiya and S. Koda, Chem. Phys. **113**, 271 (1987).
5. D. T. Cramb, S. C. Wallace and H. Bitto, Chem. Phys. Lett. **206**, 515 (1993).
6. K. Nishizawa, S. Kubo, A. Doi and H. Katô, J. Chem. Phys. **100**, 3394 (1994).
7. K. Ishikawa, S. Kubo and H. Katô, J. Chem. Phys. **95**, 8803 (1991).
8. G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966).
9. K. Jolma and J. Kauppinen, J. Mol. Spectrosc. **82**, 214 (1980).
10. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955, p. 286).
11. J. P. Pique, J. Manners, G. Sitja and M. Joyeux, J. Chem. Phys. **96**, 6495 (1992).
12. A. J. Merer, S. A. Morris and Ch. Jungen, J. Mol. Spectrosc. **127**, 425 (1988).