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

ATSUSHI DOI, MASAYA OHTSUKA, KIYOSHI NISHIZAWA, MASAAKI 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 V¹B₂ 00,0(K = 0) – X¹Σ⁺ 000 zero transition. Most of the extra bands may be allowed by the vibronic interaction between the V¹B₂ 00,0(K = 0) level and singlet levels, which are mostly high vibrational levels of the 1A₁(X¹Σ⁺₂⁺) 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 1A₁(X¹Σ⁺₂⁺) state and the 3A₂(3Δ_u) or/and 3B₂(3Δ_u) state.
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 6\(V\), 10\(V\) and 13\(V\) 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 15\(V\) 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 autoscan operation capability. The autoscan 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](image-url) 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 $H = 210 \text{ G}$ 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 $H = 210 \text{ G}$ 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$^1\Sigma_g^+(\pi\pi)^4$. [3] Let us express a vibrational angular momentum quantum number about the top axis originating from the degenerate bending vibration $\nu_2$ by $l$: $l = \nu_2$, $\nu_2-2$, $\nu_2-4$, ..., 1 or 0, where $\nu_2$ 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 $J$ of a rotational level, the projection of the rotational angular momentum $N$ along the molecule-fixed top axis, and the projection of $J$ 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 $^{12}$C$^{32}$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 31339–31360 and 31424 cm$^{-1}$ are classified as 15V band system. [2] We measured the excitation spectra and the Zeeman spectra in the region of 31320–31445 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 ±20%). The Forrat 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$^1\Sigma_g^+ 000'0$ 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$^1\Sigma_g^+ 011'0$ 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]
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:

$$E_0(v', J') = \frac{\sum_i [I_i(v', J' - v'', J'') E_i(v', J')] \sum_i I_i(v', J' - v'', J'')}{\sum_i I_i(v', J' - v'', J'')},$$

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]

\[
E_{Z}(JM) = -g_J \mu_B MH,
\]

where \( g_J \) is a g-factor of a \( JM \) level, \( \mu_B \) 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 \( \mu_J \) of a \( J \) level can be evaluated by \( [J(J + 1)]^{1/2} g_J \), in units of Bohr magneton, 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 \( \text{cm}^{-1} \). \( I \) is the relative line intensity. \( g_J \) and \( \mu_J \) are, respectively, g-factor and the magnetic moment (in units of Bohr magneton) of upper level.

| \( J' \) | \( P(J' + 1) \) | \( I \) | \( g_J \) | \( Q(J') \) | \( I \) | \( g_J \) | \( R(J' – 1) \) | \( I \) | \( g_J \) | \( \mu_J \) |
|---|---|---|---|---|---|---|---|---|---|---|
| 31325.3 band |
| 1 | 31324.8317 | 94 | 0.02 | 31325.4858 | 61 | 0.02 | 0.07 |
| 3 | 31324.4970 | 118 | 0.02 | 31326.0283 | 101 | 0.02 | 0.07 |
| 5 | 31324.1310 | 85 | 0.02 | 31326.5307 | 35 | 0.02 | 0.13 |
| 7 | 31323.8547 | 85 | 31327.1292 | 37 | 0.02 | 0.13 |
| 9 | 31323.6332 | 67 | 31327.7819 | 46 | 0.02 | 0.13 |
| 31329.9 band |
| 1 | 31329.4523 | 36 | 31330.1037 | 37 | 0.02 | 0.13 |
| 3 | 31329.1598 | 42 | 31330.6814 | 68 | 0.02 | 0.13 |
| 5 | 31328.8713 | 29 | 31331.2737 | 60 | 0.02 | 0.13 |
| 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 | 0.02 | 0.13 |
| 1 | 31344.5962 | 25 | 31345.2481 | 16 | 0.02 | 0.13 |
| 3 | 31344.2462 | 413 | 31345.7723 | 275 | 0.02 | 0.13 |
| 3 | 31344.3095 | 20 | 31345.8355 | 17 | 0.02 | 0.13 |
| 5 | 31343.1988 | 89 | 31345.5988 | 93 | 0.02 | 0.13 |
| 5 | 31343.5245 | 148 | 31345.9246 | 140 | 0.02 | 0.13 |
| 5 | 31344.0394 | 281 | 31346.4396 | 329 | 0.02 | 0.13 |
| 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 | 0.02 | 0.13 |
| 9 | 31342.5184 | 141 | 31346.6664 | 180 | 0.02 | 0.13 |
| 9 | 31343.3103 | 67 | 31347.4591 | 53 | 0.02 | 0.13 |
| 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 | 0.02 | 0.13 |
| 3 | 31379.4850 | 23 | 31381.0155 | 21 | 0.02 | 0.13 |
| 5 | 31379.0241 | 41 | 0.02 | 31381.4258 | 45 | 0.02 | 0.13 |
| 7 | 31378.7730 | 47 | 0.02 | 31382.0460 | 54 | 0.02 | 0.13 |
| 9 | 31378.5521 | 19 | 0.01 | 31382.6939 | 25 | 0.02 | 0.14 |
Table I (Cont’d)

| \(J'\) | \(P(J' + 1)\) | \(l\) | \(\alpha_r\) | \(Q(J')\) | \(l\) | \(\alpha_r\) | \(R(J' - 1)\) | \(l\) | \(\alpha_r\) | \(\mu_r\) |
|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 31377.5831 | 13 | 31389.6 band | 31382.5987 | 31 |
| 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 |
| 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 |
| 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 |
| 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 |
| 1  | 31410.3681 | 43 | 31411.0218 | 45 |
| 3  | 31410.0072 | 57 | 31411.5378 | 60 |
| 5  | 31409.4947 | 69 | 31411.8950 | 71 |
| \(J'\) | \(P(J' + 1)\) | \(I\) | \(\omega_r\) | \(Q(J')\) | \(I\) | \(\omega_r\) | \(R(J' - 1)\) | \(I\) | \(\omega_r\) | \(\mu_r\) |
|------|--------|------|--------|--------|------|--------|--------|------|--------|--------|
| 7    | 31409.1099 | 37   |        |        |      |        |        |      |        |        |
| 7    | 31409.0029 | 22   | 0.01   |        |      |        |        |      |        |        |
| 7    | 31409.1515 | 21   |        |        |      |        |        |      |        |        |
| 9    | 31408.6113 | 48   |        |        |      |        |        |      |        |        |
| 11   | 31407.7547 | 49   |        |        |      |        |        |      |        |        |
| 11   | 31408.5914 | 27   |        |        |      |        |        |      |        |        |
| 15   | 31406.8666 | 24   |        |        |      |        |        |      |        |        |
| 15   | 31407.0580 | 22   |        |        |      |        |        |      |        |        |
|      |          |      |        |        |      |        |        |      |        |        |
|      | 31420.2 band | |        |        |      |        |        |      |        |        |
| 1    | 31419.6983 | 116  | 0.05   |        |      |        |        |      |        |        |
| 3    | 31419.3787 | 179  |        |        |      |        |        |      |        |        |
| 5    | 31418.8299 | 65   | 0.04   |        |      |        |        |      |        |        |
| 5    | 31419.0294 | 211  |        |        |      |        |        |      |        |        |
| 7    | 31418.5890 | 85   |        |        |      |        |        |      |        |        |
| 9    | 31417.3896 | 81   | 0.01   |        |      |        |        |      |        |        |
| 9    | 31418.2853 | 32   | 0.01   |        |      |        |        |      |        |        |
| 11   | 31417.4611 | 171  |        |        |      |        |        |      |        |        |
| 13   | 31416.9963 | 44   |        |        |      |        |        |      |        |        |
| 13   | 31417.0566 | 53   |        |        |      |        |        |      |        |        |
| 15   | 31416.3093 | 42   |        |        |      |        |        |      |        |        |
| 15   | 31416.4899 | 28   |        |        |      |        |        |      |        |        |
| 17   | 31416.0766 | 26   |        |        |      |        |        |      |        |        |
|      |          |      |        |        |      |        |        |      |        |        |
|      | 31422.2 band | |        |        |      |        |        |      |        |        |
| 1    | 31421.8665 | 31   |        |        |      |        |        |      |        |        |
| 3    | 31421.3078 | 40   | 0.02   |        |      |        |        |      |        |        |
| 5    | 31421.0660 | 36   | 0.03   |        |      |        |        |      |        |        |
| 7    | 31420.6700 | 28   | 0.03   |        |      |        |        |      |        |        |
| 7    | 31420.8605 | 49   | 0.05   |        |      |        |        |      |        |        |
| 9    | 31420.3687 | 30   |        |        |      |        |        |      |        |        |
| 9    | 31420.5322 | 57   | 0.03   |        |      |        |        |      |        |        |
| 11   | 31420.0774 | 58   |        |        |      |        |        |      |        |        |
|      |          |      |        |        |      |        |        |      |        |        |
|      | 31427.3 band | |        |        |      |        |        |      |        |        |
| 1    | 31426.8380 | 47   |        |        |      |        |        |      |        |        |
| 3    | 31426.3225 | 19   |        |        |      |        |        |      |        |        |
| 3    | 31426.5621 | 52   |        |        |      |        |        |      |        |        |
| 5    | 31426.4022 | 21   | 0.01   |        |      |        |        |      |        |        |
| 7    | 31425.4493 | 89   | 0.02   |        |      |        |        |      |        |        |
| 7    | 31425.7956 | 24   | 0.02   |        |      |        |        |      |        |        |
| 9    | 31425.4089 | 45   | 0.01   |        |      |        |        |      |        |        |
| 11   | 31424.4922 | 15   |        |        |      |        |        |      |        |        |
| 11   | 31425.1986 | 46   | 0.01   |        |      |        |        |      |        |        |
| 13   | 31424.5402 | 24   |        |        |      |        |        |      |        |        |
|      |          |      |        |        |      |        |        |      |        |        |
|      | 31440.3 band | |        |        |      |        |        |      |        |        |
| 1    | 31439.9178 | 17   | 0.11   |        |      |        |        |      |        |        |
| 3    | 31439.3425 | 25   | 0.03   |        |      |        |        |      |        |        |
| 5    | 31439.0229 | 25   | 0.01   |        |      |        |        |      |        |        |
| 7    | 31438.4132 | 30   | 0.01   |        |      |        |        |      |        |        |
| 9    | 31438.0629 | 38   |        |        |      |        |        |      |        |        |
| 11   | 31437.7330 | 34   |        |        |      |        |        |      |        |        |
| 13   | 31437.2847 | 19   | 0.02   |        |      |        |        |      |        |        |
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 $B_v$ |
|------|-------------|-----------------|------|-------------|-----------------|
| 1    | 31325.4861  | $G_v = 31325.2709(142)$ | 1    | 31392.5172  | $G_v = 31788.3945(361)$ |
| 3    | 31326.6813  | $B_v = 0.1151(3)$ | 2    | 31789.0499  | $B_v = 0.1194(7)$ |
| 5    | 31328.7137  | 3               | 3    | 31789.8546  | 4               |
| 7    | 31331.7120  | 4               | 7    | 31790.8398  | 5               |
| 9    | 31335.6378  | 5               | 6    | 31792.0397  | 7               |
| 71329.9 band | 6        | 71329.31054     | 7    | 31793.4711  | 8               |
| 3    | 31788.3945  | $G_v = 31329.8822(280)$ | 8    | 31797.0013  | 9               |
| 5    | 31331.3392  | $B_v = 0.1194(15)$ | 10   | 31801.4636  | 10              |
| 31333.4554  | 11       | 31336.2947     | 12   | 31338.5172  | 12              |
| 31340.5 band | 13       | 31338.5172     | 13   | 31341.0223  | 13              |
| 3    | 31340.7942  | 14             | 14   | 31341.2191  | 14              |
| 5    | 31341.8174  | 15             | 15   | 31341.0777  | 15              |
| 7    | 31343.8910  | 16             | 16   | 31341.9495  | 16              |
| 9    | 31346.8670  | 17             | 17   | 31342.6164  | 17              |
| 11   | 31350.7407  | 18             | 18   | 31342.5110  | 18              |
| 11   | 31355.5354  | 19             | 19   | 31342.1110  | 19              |
| 31344.9 band | 20       | 31342.6426     | 20   | 31342.0358  | 20              |
| 1    | 31345.1616  | 21             | 21   | 31342.3212  | 21              |
| 3    | 31346.4312  | 22             | 22   | 31342.5621  | 22              |
| 5    | 31348.3429  | 23             | 23   | 31342.5732  | 23              |
| 7    | 31351.3032  | 24             | 24   | 31342.4470  | 24              |
| 9    | 31355.0267  | 25             | 25   | 31342.7548  | 25              |
| 11   | 31360.3437  | 26             | 26   | 31343.4859  | 26              |
| 11   | 31365.5244  | 27             | 27   | 31343.9363  | 27              |
| 31380.4 band | 28       | 31344.0594     | 28   | 31343.5388  | 28              |
| 1    | 31380.5105  | 29             | 29   | 31342.0358  | 29              |
| 3    | 31381.6689  | 30             | 30   | 31342.5621  | 30              |
| 5    | 31383.6078  | 31             | 31   | 31342.5732  | 31              |
| 7    | 31386.6296  | 32             | 32   | 31342.4470  | 32              |
| 9    | 31390.5533  | 33             | 33   | 31342.7548  | 33              |
| 11   | 31394.6043  | 34             | 34   | 31343.4859  | 34              |
| 11   | 31398.1497  | 35             | 35   | 31343.9363  | 35              |
| 31389.6 band | 36       | 31437.1005     | 36   | 31343.9363  | 36              |
| 5    | 31392.9147  | 37             | 37   | 31342.0358  | 37              |
| 7    | 31395.8430  | 38             | 38   | 31342.5621  | 38              |
| 9    | 31399.3753  | 39             | 39   | 31342.5732  | 39              |
| 11   | 31403.9617  | 40             | 40   | 31342.4470  | 40              |
| 13   | 31409.3686  | 41             | 41   | 31342.7548  | 41              |
| 15   | 31415.8655  | 42             | 42   | 31343.4859  | 42              |
| 17   | 31423.0767  | 43             | 43   | 31343.9363  | 43              |
| 19   | 31431.2583  | 44             | 44   | 31343.9363  | 44              |
| 21   | 31440.1389  | 45             | 45   | 31343.9363  | 45              |
| 23   | 31449.9635  | 46             | 46   | 31343.9363  | 46              |
| 25   | 31460.8604  | 47             | 47   | 31343.9363  | 47              |
| 31388.9 band | 48       | 31440.5757     | 48   | 31344.02641(484) | 48              |
| 1    | 31386.0772  | $G_v = 31388.8829(662)$ | 3    | 31441.5265  | $B_v = 0.1094(5)$ |
| 3    | 31390.1598  | $B_v = 0.1085(17)$ | 5    | 31443.6086  | 5               |
| 5    | 31392.1464  | 7               | 7    | 31446.2699  | 7               |
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 $(\nu', J') - (\nu'', J' + 1)$ transition at a temperature $T$ is proportional to [8]

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

(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 $V^\dagger B_2 0\nu_20(K = 0) - X^\dagger \Sigma_g^+ 00000$ transition. Although the vibrational assignments are not conclusive, [4] Jungen et al. [2] assigned $\nu_3 = 1$ 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 $V^\dagger B_2 0\nu_20(K = 0, J' = 7)$. The upper level of the formers is assigned to a triplet state, to which transition is allowed by the spin-orbit interaction with the $V^\dagger B_2 0\nu_20(K = 0, J' = 7)$ 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 $V^\dagger B_2 0\nu_20(K = 0)$ level and a variety of rovibronic levels of the $A_2(X^\dagger \Sigma_g^+)$ and/or $A_1(X^\dagger \Sigma_g^+)$ states, which are accidentally close in energy with the $V^\dagger B_2 0\nu_20(K = 0)$ 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 $(\nu', J')-(\nu'', J' + 1)$ 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 $\chi^1 \Sigma_g^+$ ground state by exciting the $15V R(4)$ line at 31346.45 cm$^{-1}$. They identified the fluorescence lines to $\nu_3 \neq 0$, and interpreted as it is originating from the Coriolis interaction between the excited vibronic levels $VIB_2 a_1(K = 0)$ and $VIB_2 b_2(K = 1)$. 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 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 cm$^{-1}$ (see Fig. 2). We found two extra $R(4)$ lines at 31345.5988 and 31345.9246 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 $^3A_2(^3\Delta_o)$, which is allowed by the spin-orbit interaction with the $VIB_2 00_2 0(K = 0)$ 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 \( \nu_2 \) 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 \( V^1B_2 \ 0\nu_2 \ 0 \ (K = 0) \) level and singlet states. \( \text{CS}_2 \) has normal vibrations of the symmetry \( A_i(\nu_1 \ \text{and} \ \nu_2) \) and \( B_2(\nu_3) \). 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 ± 130 cm\(^{-1}\). [11] Therefore, most of the extra bands may be allowed by the vibronic interaction between the \( V^1B_2 \ 0\nu_2 \ 0 \ (K = 1) \) 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\(^1\) 0 level, may be allowed by the vibronic interaction between the \( V^1B_2 \ 0\nu_2 \ 0 \ (K = 1) \) 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 \( V^1B_2 \ 0\nu_2 \ 0 \ (K = 0) \) 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 (\( \pi_\gamma \pi_\mu \)) [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 15\( V \) band system. The 31344.9 band, which is the strongest band of the 15\( V \) 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. Kleman, 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).