# The Infrared Spectrum of $CS_2$ in the $\nu_3$ Band Region

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A total number of 24 bands of the carbon disulfide isotopomers $^{32}S_2{}^{12}C$, $^{34}S^{12}C^{32}S$, $^{33}S^{12}C^{32}S$, $^{34}S_2{}^{12}C$, $^{32}S_2{}^{13}C$, and $^{34}S^{13}C^{32}S$ between 1555 and 1455 cm$^{-1}$ have been investigated. Vibrational frequencies and rotational constants have been determined for the bands.

Recently, the $\nu_3$ band system of $CS_2$ has been studied by laser diode spectroscopy [1]. However, several parts of the stronger line series and many weaker bands were not measured. Here an extended analysis of the fundamental and of the associated hot bands shall be reported. We also include data on additional bands of isotopic forms of the molecule in natural abundance.

Two spectra of $CS_2$ have been evaluated, both recorded with a BOMEM DA 3.002 spectrometer at an apodized resolution of 0.004 cm$^{-1}$, cell length 15 cm, room temperature, and pressure appr. 65 Pa (0.5 Torr). Residual $H_2O$ lines in the spectra were used to calibrate the line frequencies using the data of Guelachvili [2]. Due to the limited number of usable $H_2O$ lines within the spectral range studied, the absolute accuracy of the vibrational frequencies given in Tables 1 and 2 is limited to $\pm 3 \cdot 10^{-4}$ cm$^{-1}$ (one standard error). The rotational constants in the tables are not influenced to any measurable extent by this problem.

Bands of several types were observed, such as $\Sigma_u^+ \leftarrow \Sigma_g^+$, $\Sigma_g^+ \leftarrow \Sigma_u^+$, $\Pi_g \leftarrow \Pi_u$, $\Delta_u \leftarrow \Delta_g$, and $\Phi_g \leftarrow \Phi_u$ (for the unsymmetrical species g and u are to be omitted). The assignment of the stronger bands in the spectrum was straightforward, because either the band center or the rotational constants (or both) were known from earlier investigations [1, 3–8]. Weak bands were identified from Loomis-Wood plots of the type described in [9], and a provisional J-numbering modified to give effective B-constants in agreement with expectation. The missing lines in the bands of the symmetric isotopomers were also of help in the assignment.

Some difficulty was experienced in the case of weak bands with unobservable $l$-type doubling of the lines. Such bands ($03^3 1 \leftarrow 03^3 0$ and $12^2 1 \leftarrow 12^2 0$ of $^{32}S_2{}^{12}C$) look like bands of the unsymmetrical isotopomers. However, by considering the relative intensities of the line series it was possible to assign all bands down to a common intensity limit corresponding to appr. 0.05% abundance. The $^{13}CS_2$ bands are weak, but presented no assignment problems because they are not overlapped much by $^{12}CS_2$ bands.

Only one $Q$ branch was intense enough to be observed, belonging to the $^{32}S_2{}^{12}C$ $02^2 1 \leftarrow 02^2 0$ transition. $Q(2)$ to $Q(10)$ were seen, but not included in the rotational constant fit.

All observed bands were of the type $\Delta l = 0$, and a method of evaluation similar to that of [1] was chosen. The line frequencies were fitted to a polynomial

$$\begin{aligned}\nu_0 = \nu_c &+ (B''_{\text{eff}} + B'_{\text{eff}})\, m \\ &+ (-B''_{\text{eff}} + B'_{\text{eff}} + D''_{\text{eff}} - D'_{\text{eff}})\, m^2 \\ &- 2(D''_{\text{eff}} + D'_{\text{eff}})\, m^3 + (D''_{\text{eff}} - D'_{\text{eff}})\, m^4, \quad (1)\end{aligned}$$

where $m = J'' + 1$ for R branch and $m = -J''$ for P branch lines. An attempt to determine $H_{\text{eff}}$ through inclusion of a $m^5$ term in (1) was unsuccessful for all bands ($H_{\text{eff}} < 10^{-14}$ cm$^{-1}$).

Within our level of accuracy the effective rotational constants (subscript eff) can be reduced by means of the equations

$$B_v = B_{\text{eff}} - 2l^2 D_{\text{eff}} \pm 1/2\, q_v, \quad (2)$$

$$D_v = D_{\text{eff}} \pm 1/2\, q_{1v}, \quad (3)$$

$$q_v = B_{\text{eff}}(f) - B_{\text{eff}}(e), \quad (4)$$

$$q_{1v} = D_{\text{eff}}(f) - D_{\text{eff}}(e). \quad (5)$$

Finally, the vibrational term difference is given by

$$\nu_0 = \nu_c + (B'_{\text{eff}} - B''_{\text{eff}})\, l^2. \quad (6)$$

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Table 1. Band centers and effective rotational constants for the $\nu_3$ region in cm$^{-1}$. One standard error is given in parenthesis in units of last digit.
[a] This work: 136. – Some higher $J$ lines from [1] included. [b] This work: 93. [c] This work: 113. [d] Equal to $D'_{\mathrm{eff}}$

| | $\nu_c$ | $B'_{\mathrm{eff}}$ | $B''_{\mathrm{eff}}$ | $(B'-B'')_{\mathrm{eff}} \times 10^4$ | $D'_{\mathrm{eff}} \times 10^8$ | $D''_{\mathrm{eff}} \times 10^8$ | $(D'-D'')_{\mathrm{eff}} \times 10^{12}$ | $R(J)$-range | $P(J)$-range |
|---|---|---|---|---|---|---|---|---|---|
| $^{32}S^{12}C^{32}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1535.35652 (3) | 0.10841279 (29) | 0.10912555 (29) | −7.12757 (9) | 1.1759 (11) | 1.1756 (11) | 2.92 (47) | 0 to 164[a] | 2 to 136 |
| $01^1 1e \leftarrow 01^1 0e$ | 1528.89470 (4) | 0.10859126 (41) | 0.10930090 (41) | −7.09643 (18) | 1.1987 (21) | 1.1979 (21) | 7.5 (14) | 1 to 121 | 3 to 121 |
| $01^1 1f \leftarrow 01^1 0f$ | 1528.89476 (4) | 0.10866781 (37) | 0.10937822 (37) | −7.10415 (17) | 1.2034 (20) | 1.2027 (20) | 7.6 (13) | 2 to 120 | 2 to 120 |
| $10^0 1 \leftarrow 10^0 0$ | 1527.46886 (5) | 0.10825985 (52) | 0.10897044 (52) | −7.10592 (26) | 1.1989 (36) | 1.1956 (36) | 32.3 (24) | 2 to 104 | 2 to 116 |
| $02^0 1 \leftarrow 02^0 0$ | 1522.68180 (5) | 0.10878248 (53) | 0.10949331 (53) | −7.10835 (29) | 1.1167 (41) | 1.1162 (41) | 5.5 (31) | 8 to 96 | 2 to 106 |
| $02^2 1e \leftarrow 02^2 0e$ | 1522.44228 (4) | 0.10884435 (40) | 0.10955160 (40) | −7.07249 (23) | 1.2840 (32) | 1.2857 (32) | −17.0 (26) | 4 to 94 | 4 to 100 |
| $02^2 1f \leftarrow 02^2 0f$ | 1522.44241 (4) | 0.10884359 (42) | 0.10955087 (42) | −7.07278 (23) | 1.2198 (33) | 1.2187 (33) | 11.4 (25) | 3 to 99 | 3 to 101 |
| $11^1 1e \leftarrow 11^1 0e$ | 1520.86710 (5) | 0.10847152 (76) | 0.10917772 (76) | −7.06197 (42) | 1.2576 (86) | 1.2527 (86) | 48.3 (68) | 1 to 79 | 3 to 91 |
| $11^1 1f \leftarrow 11^1 0f$ | 1520.86707 (5) | 0.10855596 (60) | 0.10926241 (60) | −7.06448 (38) | 1.2354 (58) | 1.2305 (58) | 48.5 (52) | 2 to 90 | 4 to 88 |
| $03^1 1e \leftarrow 03^1 0e$ | 1516.38107 (6) | 0.10888384 (77) | 0.10959233 (77) | −7.08493 (52) | 1.1834 (100) | 1.1849 (100) | −15.3 (89) | 3 to 79 | 5 to 81 |
| $03^1 1f \leftarrow 03^1 0f$ | 1516.38103 (8) | 0.10902788 (94) | 0.10973844 (94) | −7.10561 (64) | 1.1640 (103) | 1.1655 (103) | −14.7 (100) | 6 to 80 | 6 to 82 |
| $03^3 1 \leftarrow 03^3 0$ | 1515.99964 (4) | 0.10905744 (44) | 0.10976200 (44) | −7.04562 (32) | 1.2674 (51) | 1.2677 (51) | −3.4 (49) | 3 to 86 | 9 to 83 |
| $20^0 1 \leftarrow 20^0 0$ | 1519.49511 (8) | 0.1081191 (16) | 0.1088265 (16) | −7.07448 (39) | 1.274 (26) | [d] | | 6 to 68 | 2 to 68 |
| $12^0 1 \leftarrow 12^0 0$ | 1514.68607 (12) | 0.1086768 (25) | 0.1093846 (25) | −7.07786 (59) | 0.725 (35) | [d] | | 4 to 74 | 10 to 68 |
| $12^2 1 \leftarrow 12^2 0$ | 1514.32680 (7) | 0.1087568 (14) | 0.1094598 (14) | −7.02982 (37) | 1.329 (26) | [d] | | 5 to 62 | 11 to 62 |
| $00^0 2 \leftarrow 00^0 1$ | 1522.27126 (9) | 0.1076988 (18) | 0.1084108 (18) | −7.11987 (39) | 1.108 (24) | [d] | | 3 to 69 | 9 to 77 |
| $^{33}S^{12}C^{32}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1533.56450 (3) | 0.10676742 (37) | 0.10746913 (37) | −7.01710 (14) | 1.1393 (36) | 1.1386 (36) | 6.8 (16) | 1 to 121[b] | 5 to 89 |
| $01^1 1e \leftarrow 01^1 0e$ | 1527.11249 (13) | 0.1069467 (19) | 0.1076455 (19) | −6.98738 (54) | 1.222 (31) | [d] | | 23 to 65 | 18 to 70 |
| $01^1 1f \leftarrow 01^1 0f$ | 1527.11253 (8) | 0.1070173 (11) | 0.1077168 (11) | −6.99469 (30) | 1.145 (16) | [d] | | 25 to 71 | 22 to 75 |
| $^{34}S^{12}C^{32}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1531.89247 (3) | 0.10521605 (27) | 0.10590739 (27) | −6.91332 (9) | 1.1098 (16) | 1.1096 (16) | 1.72 (68) | 3 to 145[c] | 2 to 112 |
| $01^1 1e \leftarrow 01^1 0e$ | 1525.44992 (6) | 0.10539130 (51) | 0.10607970 (51) | −6.88397 (32) | 1.1395 (43) | 1.1388 (43) | 6.8 (38) | 2 to 8 &<br>25 to 91 | 2 to 5 &<br>28 to 95 |
| $01^1 1f \leftarrow 01^1 0f$ | 1525.44977 (7) | 0.10546017 (65) | 0.10614923 (65) | −6.89058 (42) | 1.1101 (59) | 1.1095 (59) | 5.6 (52) | 3 to 7 &<br>26 to 90 | 2 to 9 &<br>25 to 92 |
| $10^0 1 \leftarrow 10^0 0$ | 1524.16652 (7) | 0.10506435 (89) | 0.10575391 (89) | −6.89569 (63) | 1.1083 (105) | 1.1057 (105) | 25.8 (105) | 5 to 78 | 3 to 83 |
| $02^0 1 \leftarrow 02^0 0$ | 1519.23495 (7) | 0.1055836 (14) | 0.1062725 (14) | −6.88890 (40) | 1.086 (24) | [d] | | 3 to 72 | 3 to 61 |
| $02^2 1 \leftarrow 02^2 0$ | 1519.01654 (5) | 0.10563329 (87) | 0.10631948 (87) | −6.86189 (20) | 1.161 (11) | [d] | | 5 to 81 | 5 to 79 |
| $^{34}S^{12}C^{34}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1528.37165 (6) | 0.10204679 (91) | 0.10271697 (91) | −6.70182 (19) | 1.0253 (103) | [d] | | 2 to 84 | 4 to 80 |
| $^{32}S^{13}C^{32}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1485.33175 (3) | 0.10844377 (38) | 0.10912968 (38) | −6.85908 (22) | 1.1729 (34) | 1.1728 (34) | 0.7 (28) | 0 to 90 | 2 to 96 |
| $01^1 1e \leftarrow 01^1 0e$ | 1479.31796 (4) | 0.10860926 (71) | 0.10929222 (71) | −6.82962 (17) | 1.1784 (109) | [d] | | 5 to 73 | 3 to 69 |
| $01^1 1f \leftarrow 01^1 0f$ | 1479.31787 (4) | 0.10868938 (68) | 0.10937309 (68) | −6.83714 (15) | 1.1925 (96) | [d] | | 4 to 72 | 6 to 72 |
| $10^0 1 \leftarrow 10^0 0$ | 1477.63182 (12) | 0.1083020 (23) | 0.1089848 (23) | −6.82804 (94) | 1.204 (67) | [d] | | 16 to 46 | 12 to 54 |
| $^{34}S^{13}C^{32}S$ | | | | | | | | | |
| $00^0 1 \leftarrow 00^0 0$ | 1481.74509 (10) | 0.1052400 (18) | 0.1059050 (18) | −6.65058 (77) | 0.914 (55) | [d] | | 16 to 49 | 16 to 54 |

Table 2. Band origins and rotational constants in $cm^{-1}$ for bands with $l \neq 0$.

| | $\nu_0$ | $B'$ | $B''$ | $q' \times 10^5$ | $q'' \times 10^5$ | $(q' - q'') \times 10^7$ |
|---|---|---|---|---|---|---|
| $^{32}S^{12}C^{32}S$ | | | | | | |
| $01^11 \leftarrow 01^10$ | 1528.89402(4) | 0.1086295 (4) | 0.1093395 (4) | 7.655 (55) | 7.732 (55) | −7.72(25) |
| $02^21 \leftarrow 02^20$[a] | 1522.43952(4) | 0.1088439 (4) | 0.1095511 (4) | −0.076 (58) | −0.073 (58) | 0.29(33) |
| $11^11 \leftarrow 11^10$ | 1520.86638(5) | 0.1085137 (7) | 0.1092200 (7) | 8.444 (97) | 8.469 (97) | −2.51(57) |
| $03^11 \leftarrow 03^10$ | 1516.38034(6) | 0.1089558 (8) | 0.1096654 (8) | 14.404(122) | 14.611(122) | −20.68(82) |
| $03^31 \leftarrow 03^30$ | 1515.99753(4) | 0.1090572 (4) | 0.1097618 (4) | | | |
| $12^21 \leftarrow 12^20$ | 1514.32399(7) | 0.1087567(14) | 0.1094597(14) | | | |
| $^{33}S^{12}C^{32}S$ | | | | | | |
| $01^11 \leftarrow 01^10$ | 1527.11181(8) | 0.1069820(15) | 0.1076811(15) | 7.06 (22) | 7.13 (22) | −7.31(61) |
| $^{34}S^{12}C^{32}S$ | | | | | | |
| $01^11 \leftarrow 01^10$ | 1525.44916(6) | 0.1054257 (6) | 0.1061144 (6) | 6.887 (83) | 6.953 (83) | −6.61(53) |
| $02^21 \leftarrow 02^20$ | 1519.01380(5) | 0.1056332 (9) | 0.1063194 (9) | | | |
| $^{32}S^{13}C^{32}S$ | | | | | | |
| $01^11 \leftarrow 01^10$ | 1479.31723(4) | 0.1086493 (7) | 0.1093326 (7) | 8.012 (98) | 8.087 (98) | −7.52(23) |

One standard error is given in parenthesis in units of last digit.
For definitions, see Eq. (2)–(6) in text

| [a] $^{32}S^{12}C^{32}S$ | $q_1' \times 10^{12}$ | $q_1'' \times 10^{12}$ | $(q_1' - q_1'') \times 10^{12}$ |
|---|---|---|---|
| $02^21 \leftarrow 02^20$ | −642(46) | −670(46) | 28.4(36) |

Table 3. Calculated band constants for the $10^00 \leftarrow 00^00$ transition and comparison with literature values. One standard error is given in parenthesis in units of last digit. [a] Ref. [7, 10]. [b] Ref. [6]. [c] For the $10^00 \leftarrow 01^10$ bands, no significant $\Delta D$ value was found.

| Isotopomer | $^{32}S^{12}C^{32}S$ | $^{34}S^{12}C^{32}S$ | $^{33}S^{12}C^{32}S$ | $^{32}S^{13}C^{32}S$ | $^{34}S^{13}C^{32}S$ |
|---|---|---|---|---|---|
| $\nu_0(10^00 \leftarrow 00^00)$ ($cm^{-1}$) | 658.0003 (6)<br>657.9982 (3)[a] | 648.6071(5) | 653.1912(6) | 657.23387(12)<br>657.2347 (5)[b] | 647.97346(17) |
| $B_{10^00} - B_{00^00}$ ($10^{-4}\,cm^{-1}$) | −1.5532 (6)<br>−1.555 (3)[a] | −1.5206(5) | −1.5377(7) | −1.4314 (6)<br>−1.439 (5)[b] | −1.4225 (12) |
| $D_{10^00} - D_{00^00}$ ($10^{-12}\,cm^{-1}$) | 247 (4)<br>170 (40)[a] | 231 (4) | 230 (7) | 340 (6)<br>≈170[b,c] | ≈280 |

The results are tabulated in Tables 1 and 2*. Because of the very large number of previous investigations, a detailed comparison with literature values shall not be given here (see [1, 3, 11] for a survey of papers on $CS_2$). Generally, the precision of the constants in Table 1 and 2 has been improved considerably. As an example, in Table 3 we have calculated the infrared-inactive $10^00 \leftarrow 00^00$ transition of several isotopomers from our data on the $00^01 \leftarrow 00^00$ bands combined with laser-diode data on the $00^01 \leftarrow 10^00$ bands [8, 11]. Table 3 also includes constants for $^{12}C^{32}S_2$ and $^{13}C^{32}S_2$ obtained from the $01^10 \leftarrow 00^00$ and $10^00 \leftarrow 01^10$ bands, which have been measured with similar precision [6, 7, 10].

The agreement of the $10^00$ vibrational terms is within three times the combined standard errors. However, it should be remembered that our absolute frequency accuracy is about $\pm 3 \cdot 10^{-4}\,cm^{-1}$ as stated above. This value must be added to the standard errors of $\nu_0$ in Table 3. Older determinations of $10^00$ level data from grating spectra (e.g. [5]) yield $\nu_0$ and $\Delta B$ values of somewhat lower precision but no significant $\Delta D$ values. – In conclusion, the present investigation has greatly improved our knowledge of the molecular constants of $CS_2$, at the same time showing the high information content of a modern Fourier transform spectrum.

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* A table of all evaluated line frequencies has been deposited under no. TNA 14 in the University Library of Kiel, and copies may be obtained there or from the authors.

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