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# Microwave Spectra and Equilibrium Structure of Carbonyl Sulfide

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Microwave spectra have been measured for various vibrationally excited states of the OCS molecule. The *l*-type doubling constants obtained for the excited states of the bending vibration, $\nu_2$, have led to the determination of the zero-order coupling constant, $q_e$. It has been shown that the $q_e$ value thus obtained is useful for the evaluation of the harmonic force constants. The Fermi resonances have been discussed; they lead to the conclusion that the effect due to the cubic constant, $k_{223}$, cannot be ignored, nor can that due to $k_{122}$. With due consideration for this situation, the equilibrium structure has been found to be:

$r_e(\text{O–C})=1.157_2\pm0.002$ Å and $r_e(\text{C–S})=1.560_6\pm0.002$ Å.

The microwave spectrum of carbonyl sulfide has been studied by many investigators, and the $r_0$ and $r_s$ structures have been determined from the spectrum in the ground vibrational state.[1,2] The spectra in the excited vibrational states, however, have not been investigated completely enough to determine the equilibrium structure. The chief difficulty is the weakness of the spectral lines in the vibrationally excited states, in particular in the excited state of the $\nu_3$ vibration, whose frequency is as high as 2000 cm$^{-1}$. In order to determine the $r_e$ structure, the rotational transitions in the first excited states of the three normal vibrations ($\nu_1=859$, $\nu_2=520$, $\nu_3=2062$ cm$^{-1}$) must be observed, at least for two isotopic species. Since the Boltzmann factor of the $\nu_3$ exicted state is about $4\times10^{-5}$ and since the natural abundance of $^{34}$S is 4%, the spectrometer must be sensitive enough to detect a spectral line $1.6\times10^{-6}$ times as strong as the line of the normal species in the ground vibrational state. This requirement has been met by the improvement of the sensitivity of the spectrometer and by the development of a high-temperature cell.

The analysis of the Fermi resonance interaction is important for the determination of the $r_e$ structure, since the unperturbed $\alpha$ value must be known in order to obtain the equilibrium rotational constants. The $r_e$ structure of the carbonyl sulfide molecule has been determined by Callomon and Thompson[3] from an analysis of the infrared spectrum, but their treatment of the Fermi resonance was not satisfactory. The purpose of the present study is to determine the precise $r_e$ structure of carbonyl sulfide by eliminating the Fermi resonances.

## Experimental

The sample was prepared by mixing a saturated aqueous solution of ammonium thiocyanate with sulfuric acid.[4] The gas thus evolved was passed through a concentrated aqueous solution of sodium hydroxide to remove such impurities as $NH_3$, $H_2S$, $CO_2$ and HCN, and then a trace of moisture was eliminated with calcium chloride.

The spectrometer used was of a conventional Stark-modulation type. The cell was made so that it could be heated up to about 250°C in order to observe the spectra in the vibrationally excited states. As the intensity of a microwave absorption line for a linear molecule is proportional to,[5]

$$T^{-5/2}\exp(-h\nu/\boldsymbol{k}T), \tag{1}$$

a line in the level of 2000 cm$^{-1}$ (the $\nu_3$ state, for example) is about 10 times stronger at 200°C than at room temperature. It can, however, easily be seen that the increase in the intensity with the temperature becomes gradually smaller above 200°C. Therefore, in order to detect a weak line in an excited state, it is more effective to improve the sensitivity of the spectrometer at a high temperature than to raise the temperature more. For measuring an absorption line in a level above 3000 cm$^{-1}$, the cell must be raised above 250°C, but no suitable materials have been found for making a electrode supporter with a small attenuation and a small reflection for microwaves at high temperatures. Considering this situation, together with the fact that carbonyl sulfide begins to decompose at 250°C, the high-temperature work above 250°C was abandoned.

The sweep rate was made slow in order to increase the sensitivity of the spectrometer. It requires a microwave source which is stable over a long period. Sufficient stability has been attained by using the simple oil-bath cooling of the Varian Klystron X-13, without any AFC or any phase-lock system. The minium detectable absorption coefficient was $3\times10^{-10}$ cm$^{-1}$ at 24000

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[1] C. H. Townes, A. N. Holden and F. R. Merritt, *Phys. Rev.*, **74**, 1113 (1948).

[2] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

[3] H. J. Callomon and H. W. Thompson, *Proc. Roy. Soc.*, **A222**, 431 (1954).

[4] G. Brauer, "Handbuch der präparativen anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart.

[5] T. Oka, K. Takagi and Y. Morino, *J. Mol. Spectry.*, **14**, 27 (1964).

Mc/sec; it was attained by a sweep rate of about 0.1 Mc/sec per minute, with a band width of 0.05 cps.

The frequency measurement was perforemd by using a VHF (200—250 Mc/sec) vacuum-tube oscillator and a 2.5 Mc crystal oscillator. The latter frequency was checked regularly against the 5 Mc/sec JJY broadcast. The beat signal of VHF with harmonics of 2.5 Mc/sec was displayed on an oscilloscope when the VHF oscillator was slightly frequency-modulated by a 10 cps saw-tooth signal of the oscilloscope through a variable-capacitance diode. The beat frequency of the microwave and the harmonics of the VHF were shown on the same oscilloscope after being received by an all-wave receiver. This device is useful not only in minimizing the error of the frequency measurement in the slow-sweep recording, but also in monitoring the stability of the microwave frequency sweeping.

## Results

The observed frequencies of the $J=1\leftarrow 0$, $2\leftarrow 1$, $3\leftarrow 2$ and $5\leftarrow 4$ transitions for various excited vibrational states of the $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ and $^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}$ molecules are listed in Tables 1 and 2. Although some of these lines had already been measured by Low[6] and others, precise measurements were carried out again for the whole series of rotational transitions, because small systematic deviations in the frequencies of some individual lines are serious for the consideration of $\alpha_v$ or $q_v$ in the series of excited vibrational states. The $J=2\leftarrow 1$ transitions were mainly used for the calculation of the molecular constants, as will be described below. Other transitions were used when the $J=2\leftarrow 1$ transition was missing, or when confirmation was necessary. The rotational constants, $B_v$, the vibration-rotation interaction constants, $\alpha_v$, and the $l$-type doubling constants, $q_v$, obtained from the observed frequencies are listed in Tables 3 and 4. Centrifugal corrections were made by using the value of $D=0.00131$ Mc/sec determined by King and Gordy.[7] The $\alpha_v$ constants were calculated simply by subtracting $B_v$ from $B_0$. Rigorously speaking, higher-order terms should

TABLE 1. OBSERVED MICROWAVE FREQUENCIES OF $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ (in Mc/sec)

| Vibrational state | | | Transition | | | |
|---|---|---|---|---|---|---|
| $v_1$ | $v_2^l$ | $v_3$ | $J=1\leftarrow 0$ | $J=2\leftarrow 1$ | $J=3\leftarrow 2$ | $J=5\leftarrow 4$ |
| 0 | 0 | 0 | | 24325.92 | 36488.81 | 60814.28 |
| 0 | $1^1$ | 0 | | 24355.58<br>24381.00 | 36533.38<br>36571.36 | 60888.35<br>60951.94 |
| 0 | $2^0$ | 0 | | 24400.72 | 36601.11 | 61001.48 |
| 0 | $2^2$ | 0 | | | 36615.23 | 61024.96 |
| 0 | $3^1$ | 0 | | 24409.74<br>24459.20 | | |
| 0 | $3^3$ | 0 | | | | 61128.86 |
| 0 | $4^0$ | 0 | 12229.44 | | | |
| 0 | $4^2$ | 0 | | | 36703.77 | 61172.69 |
| 0 | $4^4$ | 0 | | | | 61231.85 |
| 0 | $5^1$ | 0 | | | 36675.75<br>36784.74 | |
| 1 | 0 | 0 | | 24253.38 | | |
| 2 | 0 | 0 | | 24179.46 | | |
| 0 | 0 | 1 | | 24180.17 | | |
| 1 | $1^1$ | 0 | | 24288.36<br>24315.82 | 36432.39<br>36473.47 | 60720.4<br>60788.3 |
| 0 | $1^1$ | 1 | | | 36318.08<br>36356.78 | 60530.2<br>60594.3 |
| 1 | $3^1$ | 0 | | 24348.2<br>24400.2 | | —<br>61000.1 |
| 1 | $2^0$ | 0 | | 24337.50 | | 60843.48 |
| 1 | $2^2$ | 0 | | | 36523.38 | 60871.68 |
| 2 | $1^1$ | 0 | | 24219.54<br>24248.68 | | |

TABLE 2. OBSERVED MICROWAVE FREQUENCIES OF $^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}$ (in Mc/sec)

| Vibrational state | | | Transition | |
|---|---|---|---|---|
| $v_1$ | $v_2^l$ | $v_3$ | $J=2\leftarrow 1$ | $J=3\leftarrow 2$ |
| 0 | 0 | 0 | 23731.29 | 35596.91 |
| 0 | $1^1$ | 0 | 23760.48<br>23784.74 | 35640.66<br>35676.98 |
| 0 | $2^0$ | 0 | 23804.97 | 35707.50 |
| 0 | $2^2$ | 0 | | 35720.27 |
| 1 | 0 | 0 | 23660.56 | 35490.77 |
| 0 | 0 | 1 | 23589.52 | |
| 2 | 0 | 0 | 23588.44 | |

TABLE 3. ROTATIONAL CONSTANTS, ROTATION-VIBRATION INTERACTION CONSTANTS, AND $l$-TYPE DOUBLING CONSTANTS OF $^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}$ (in Mc/sec)

| $v_1$ | $v_2^l$ | $v_3$ | $B_v$ | $\alpha_v$ | $q_v$ |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 6081.480 | 0 | |
| 0 | $1^1$ | 0 | 6092.071 | −10.591 | 6.349 |
| 0 | $2^0$ | 0 | 6100.192 | −18.712 | |
| 0 | $2^2$ | 0 | 6102.545 | −21.065 | |
| 0 | $3^1$ | 0 | 6108.626 | −27.146 | 6.183 |
| 0 | $3^3$ | 0 | 6112.925 | −31.445 | |
| 0 | $4^0$ | 0 | 6114.723 | −33.243 | |
| 0 | $4^2$ | 0 | 6117.310 | −35.830 | |
| 0 | $4^4$ | 0 | 6123.224 | −41.744 | |
| 0 | $5^1$ | 0 | 6121.724 | −40.244 | 6.055 |
| 1 | 0 | 0 | 6063.353 | 18.127 | |
| 2 | 0 | 0 | 6044.873 | 36.607 | |
| 0 | 0 | 1 | 6045.051 | 36.429 | |
| 1 | $1^1$ | 0 | 6075.503 | 5.977 | 6.856 |
| 0 | $1^1$ | 1 | 6056.259 | 25.221 | 6.450 |
| 1 | $3^1$ | 0 | 6093.56 | −12.08 | 6.50 |
| 1 | $2^0$ | 0 | 6084.385 | −2.905 | |
| 1 | $2^2$ | 0 | 6087.227 | −5.747 | |
| 2 | $1^1$ | 0 | 6058.536 | 22.944 | 7.285 |

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6) W. Low, *Phys. Rev.*, **97**, 1664 (1955).

7) W. C. King and W. Gordy, *Phys. Rev.*, **93**, 407 (1954).

TABLE 4. ROTATIONAL CONSTANTS, VIBRATION-ROTATION INTERACTION CONSTANTS, AND $l$-TYPE DOUBLING CONSTANT OF $^{16}O^{12}C^{34}S$ (in Mc/sec)

| $v_1$ $v_2{}^l$ $v_3$ | $B_v$ | $\alpha_v$ | $q_v$ |
|---|---|---|---|
| 0 0 0 | 5932.839 | 0 | |
| 0 $1^1$ 0 | 5943.158 | −10.319 | 6.053 |
| 0 $2^0$ 0 | 5951.273 | −18.434 | |
| 0 $2^2$ 0 | 5953.392 | −20.553 | |
| 1 0 0 | 5915.152 | 17.687 | |
| 0 0 1 | 5897.390 | 35.449 | |
| 2 0 0 | 5897.120 | 35.719 | |

be included in this expanison, but they are all ignored because they are usually small. For example, $\gamma_{22}$, the second-order term for the bending vibration, was found to be so small as −0.059 Mc/sec on the assumption that $\gamma_{ll}=0$; this value was derived from the frequencies of the lines in the ($01^10$) state and in the ($02^20$) state. The assumption that $\gamma_{ll}=0$ was used for the treatments of all the Fermi resonances in this paper, though it has never been established experimentally.

**A. Fermi Resonances.** Some of the spectral lines in highly-excited states were observed at frequencies fairly different from those expected from the formula:

$$B_v = B_e - \sum_i \alpha_i\left(v_i + \frac{d_i}{2}\right). \tag{2}$$

The anomalies may be attributed mainly to Fermi resonances, although small deviations must be produced by the neglect of the higher-order terms, $\gamma_{vv'}$. Low has explained the shift of the line of $l=0$ in the $2\nu_2$ excited state by a Fermi resonance between the ($10^00$) and ($02^00$) states, and the shift of the $l=1$ line in the $3\nu_2$ state by the resonance between the two states ($11^10$) and ($03^10$). He evaluated the interaction energy for the former diad to be 43 cm$^{-1}$. A similar resonance must also be considered for the next triad, ($20^00$), ($12^00$), and ($04^00$). It turned out, however, that the calculated frequencies for the triad were in poor agreement with the observed values when the interaction energy obtained from the lower pairs were used. Therefore, another factor must be taken into account in accounting for this anomaly.

According to the theory developed by Nielsen, the vibration-rotation interaction constant, $\alpha_2$, is given by the harmonic force constants and by two cubic constants, $k_{122}$ and $k_{322}$ 8)

$$\alpha_2 = \\ -\frac{B_e}{2\pi I_e}\left(\frac{\boldsymbol{h}}{\boldsymbol{c}}\right)^{1/2}\left[2(I_e)^{1/2}\left\{\frac{\zeta_{23}{}^{(x)}}{\omega_1{}^{3/2}}k_{122} - \frac{\zeta_{21}{}^{(x)}}{\omega_3{}^{3/2}}k_{322}\right\}\right. \\ + \frac{1}{4\pi}\left(\frac{\boldsymbol{h}}{\boldsymbol{c}}\right)^{1/2}\frac{1}{\omega_2}\left\{\frac{3\omega_2{}^2+\omega_1{}^2}{\omega_2{}^2-\omega_1{}^2}(\zeta_{21}{}^{(x)})^2\right. \\ \left.\left. + \frac{3\omega_2{}^2+\omega_3{}^2}{\omega_2{}^2-\omega_3{}^2}(\zeta_{23}{}^{(x)})^2\right\}\right]. \tag{3}$$

When the observed values of $\alpha_2 = -10.767$ Mc/sec (corrected for $\gamma_{22}$) and $(\zeta_{12}{}^{(x)})^2 = 0.0225$ obtained from $q_e$ (see Section C) are put into Eq. (3), the following relation is obtained between $k_{122}$ and $k_{322}$:

$$0.29617\,k_{122} + 0.01258\,k_{322} = 13.879. \tag{4}$$

If $k_{122} = \sqrt{2}\,W_{12} = 60.8$ cm$^{-1}$ obtained by Low is put into Eq. (4), $k_{322}$ is calculated to be −328 cm$^{-1}$. Such a large value of $k_{322}$ would make it necessary to consider the interaction between the two states, ($02^00$) and ($00^01$), in addition to the resonance between the two states, ($10^00$) and ($02^00$), even if the energy difference between the two states, ($02^00$) and ($00^01$), is as large as 1000 cm$^{-1}$. Thus the perturbed energies, $E$, should be calculated by solving the secular equation:

$$\begin{vmatrix} W_1{}^0-E, & W_{12}, & 0, \\ W_{12}, & W_2{}^0-E, & W_{23}, \\ 0, & W_{23}, & W_3{}^0-E, \end{vmatrix} = 0, \tag{5}$$

where $W_i{}^0$ denotes the energy of the unperturbed state and $W_{ij}$, the interaction energy between the $i$ and $j$ states, and the subscripts 1, 2 and 3 indicate the ($00^01$), ($02^00$) and ($10^00$) states respectively. It is easily shown that the effective rotational constant, $B_i{}^*$, for a resonating state is given by: 9)

$$B_i{}^* = a_{i1}{}^2B_1{}^0 + a_{i2}{}^2B_2{}^0 + a_{i3}{}^2B_3{}^0 \tag{6}$$

where $B_i{}^0$ is the unperturbed value of the rotational constant and $a_{ij}$, the normalized transformation matrix element for the solution of Eq. (5). Rigorously speaking, $W_i{}^0$ and $W_{ij}$ should include rotational energies, 10) but if $W_i{}^0$ is approximated with the vibrational energy alone, then $k_{122}$ and $k_{322}$ are determined so as to get the best fit of the calculated $E$ and $B_i{}^*$ values with the observed values under the conditions of Eq. (4). Two sets of solutions were obtained by this calculation: one is $k_{122} = 53.5$ cm$^{-1}$ and $k_{322} = -155$ cm$^{-1}$, and the other is $k_{122} = 36.9$ cm$^{-1}$ and $k_{322} = 235$ cm$^{-1}$. Their experimental uncertainties were estimated to be 1 cm$^{-1}$ for $k_{122}$ and 15 cm$^{-1}$ for $k_{322}$.

The Fermi resonance caused by $k_{122}$ and $k_{322}$ also occurs among ($11^10$), ($03^10$), and ($01^11$); among ($12^20$), ($04^20$) and ($02^21$); among ($20^00$), ($12^00$), ($04^00$), ($10^01$), ($02^01$), and ($00^02$), and among ($21^10$), ($13^10$), ($05^10$), ($11^11$), ($03^11$), and ($01^12$). These resonances are illustrated schematically in Fig. 1, in which the lines with circles indicate new inter actions introduced by the consideration of the $k_{322}$ resonance. It may easily be seen that

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8) H. H. Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951).

9) Y. Morino, J. Nakamura and S. Yamamoto, *J. Mol. Spectry.*, **22**, 34 (1967).

10) Y. Morino and E. Hirota, This Bulletin, **31**, 423 (1958).

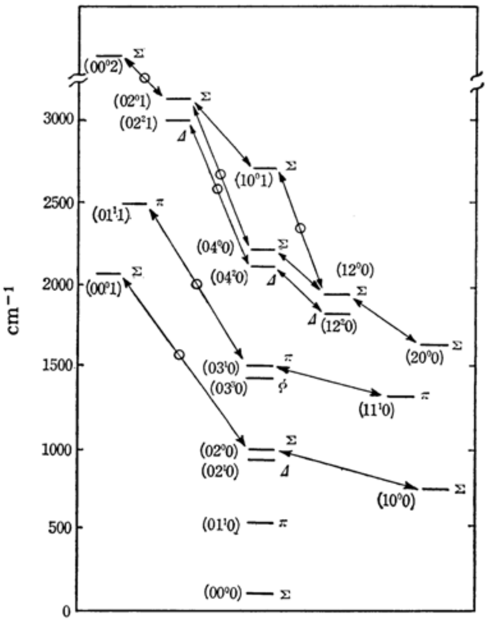

Fig. 1. Vibrational energy levels for OCS. Arrows indicate the existence of a Fermi resonance between the two states. The arrows with circles indicate the new interactions by $k_{322}$.

TABLE 5. FERMI RESONANCE PERTURBATIONS IN THE ROTATIONAL CONSTANTS OF $^{16}O^{12}C^{32}S$, WHEN $k_{122}=53.5\ \mathrm{cm}^{-1}$ AND $k_{322}=-155\ \mathrm{cm}^{-1}$ ARE USED (in Mc/sec)

| Vibrational state | | | Unperturbed | Perturbed frequency calc. | $B_{obs}-B_{calc}$ |
|---|---|---|---|---|---|
| $v_1$ | $v_2^l$ | $v_3$ | | | |
| 0 | $0^0$ | 1 | 6044.375 | 6045.053 | (−0.002) |
| 0 | $2^0$ | 0 | 6102.552 | 6100.190 | (+0.002) |
| 1 | $0^0$ | 0 | 6061.675 | 6063.280 | (+0.073) |
| 0 | $1^1$ | 1 | 6054.965 | 6056.274 | −0.015 |
| 0 | $3^1$ | 0 | 6112.928 | 6108.361 | +0.265 |
| 1 | $1^1$ | 0 | 6072.265 | 6075.523 | −0.020 |
| 0 | $2^2$ | 1 | 6065.437 | 6067.334 | |
| 0 | $4^2$ | 0 | 6123.209 | 6116.584 | +0.726 |
| 1 | $2^2$ | 0 | 6082.737 | 6087.365 | −0.138 |
| 0 | $0^0$ | 2 | 6007.260 | 6008.662 | |
| 0 | $2^0$ | 1 | 6065.437 | 6065.163 | |
| 1 | $0^0$ | 1 | 6024.560 | 6026.637 | |
| 0 | $4^0$ | 0 | 6123.209 | 6114.369 | +0.357 |
| 1 | $2^0$ | 0 | 6082.737 | 6084.554 | −0.179 |
| 2 | $0^0$ | 0 | 6041.860 | 6045.656 | −0.783 |
| 0 | $1^1$ | 2 | 6017.850 | 6020.552 | |
| 0 | $3^1$ | 1 | 6075.813 | 6074.017 | |
| 1 | $1^1$ | 1 | 6035.150 | 6039.215 | |
| 0 | $5^1$ | 0 | 6133.260 | 6120.476 | +1.248 |
| 1 | $3^1$ | 0 | 6093.113 | 6093.585 | −0.03 |
| 2 | $1^1$ | 0 | 6052.450 | 6059.790 | −1.254 |

TABLE 6. FERMI RESONANCE PERTURBATIONS IN THE ROTATIONAL CONSTANTS OF $^{16}O^{12}C^{32}S$, WHEN $k_{122}=36.9\ \mathrm{cm}^{-1}$ AND $k_{322}=235\ \mathrm{cm}^{-1}$ ARE USED (in Mc/sec)

| Vibrational state | | | Unperturbed | Perturbed frequency calc. | $B_{obs}-B_{calc}$ |
|---|---|---|---|---|---|
| $v_1$ | $v_2^l$ | $v_3$ | | | |
| 0 | 0 | 1 | 6043.434 | 6045.053 | (−0.002) |
| 0 | $2^0$ | 0 | 6102.552 | 6100.190 | (+0.002) |
| 1 | 0 | 0 | 6062.614 | 6063.280 | (+0.073) |
| 0 | $1^1$ | 1 | 6054.024 | 6057.015 | −0.753 |
| 0 | $3^1$ | 0 | 6112.928 | 6108.185 | +0.441 |
| 1 | $1^1$ | 0 | 6073.204 | 6074.956 | +0.547 |
| 0 | $2^2$ | 1 | 6064.496 | 6068.667 | |
| 0 | $4^2$ | 0 | 6123.209 | 6115.931 | +1.380 |
| 1 | $2^2$ | 0 | 6083.676 | 6086.773 | +0.554 |
| 0 | 0 | 2 | 6005.378 | 6008.875 | |
| 0 | $2^0$ | 1 | 6064.496 | 6066.068 | |
| 1 | 0 | 1 | 6024.558 | 6026.683 | |
| 0 | $4^0$ | 0 | 6123.209 | 6115.931 | −1.205 |
| 1 | $2^0$ | 0 | 6083.676 | 6084.515 | −0.130 |
| 2 | 0 | 0 | 6043.738 | 6045.321 | −0.448 |
| 0 | $1^1$ | 2 | 6015.968 | 6022.364 | |
| 0 | $3^1$ | 1 | 6074.872 | 6075.105 | |
| 1 | $1^1$ | 1 | 6035.148 | 6039.325 | |
| 0 | $5^1$ | 0 | 6133.260 | 6118.501 | +3.223 |
| 1 | $3^1$ | 0 | 6094.052 | 6094.146 | −0.59 |
| 2 | $1^1$ | 0 | 6054.328 | 6058.187 | +0.349 |

the resonance schemes are greatly complicated by the $k_{322}$ interaction. The effective $B$ values of these states were calculated in the same manner as those for the resonance among (10$^0$0), (02$^0$0) and (00$^0$1). If the set of $k_{122}=53.5\ \mathrm{cm}^{-1}$ and $k_{322}=-155\ \mathrm{cm}^{-1}$ is used, the $B$'s are calculated to be as in Table 5, where the unperturbed value, $B_v^\circ$, has been calculated by Eq. (2) by the use of the values of $\alpha_i$ corrected for the resonances. When the set of $k_{122}=36.9\ \mathrm{cm}^{-1}$ and $k_{332}=235\ \mathrm{cm}^{-1}$ is used, the $B_i$'s are calculated to be as in Table 6. The values calculated by the set of $k_{122}=53.5\ \mathrm{cm}^{-1}$ and $k_{322}=-155\ \mathrm{cm}^{-1}$ are in better agreement with the observed values than the results obtained by the other set of cubic constants. However, no sharp discrimination can be made between the two sets of cubic force constants, because the neglect of higher-order terms, $\gamma_{vv'}$ in the rotational constants might bring about the differences of the same order, and, at the same time, other higher-order resonances might influence the rotational constants.

**B. Equilibrium Structure.** Since the lines in the excited states of all the normal vibrations have been measured for the normal and $^{34}S$ species of OCS, the calculation of the equilibrium structure is possible. Of course, it is necessary, for the calculation of the equilibrium rotational constant, $B_e$, to eliminate the Fermi resonance effects from the observed values of $\alpha_v$. If the higher-order terms are ignored, the equilibrium rotational constant, $B_e$, is given by:

$$B_e = B_0 + \frac{1}{2}(\alpha_1 + \alpha_3 + 2\alpha_2), \tag{7}$$

where $2\alpha_2$ can be replaced by the $\alpha_v$ of the unperturbed $v_2=2$ state. Then $B_e$ is given by:

$$B_e = B_0 + \frac{1}{2}(\alpha^0{}_{100} + \alpha^0{}_{001} + \alpha^0{}_{02^00}), \tag{8}$$

where the superscript $^0$ designates the unperturbed values. Fortunately, these three levels interact with each other as is shown by Eq. (5), so that a sum rule holds between the perturbed and unperturbed rotational constants:

$$B_{100} + B_{001} + B_{02^00} = B^0{}_{100} + B^0{}_{001} + B^0{}_{02^00}. \tag{9}$$

This relation is shown schematically in Fig. 2, where the vector sum of the arrows which represent the Fermi shifts should be zero. Hence, $B_e$ can be calculated directly by the use of the observed values of the rotational constants, even under the Fermi resonances:

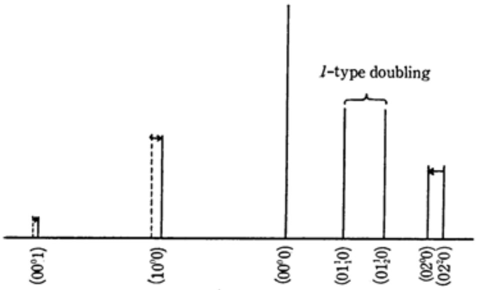

Fig. 2. The shift of the spectral lines by Fermi resonance. Broken lines denote the unperturbed positions and the arrows indicate the shifts of the rotational levels by the Fermi resonances.

$$B_e = \frac{1}{2}(5B_0 - B_{100} - B_{001} - B_{02^00}). \tag{10}$$

If a small correction by a higher-order term, $\gamma_{22}$, is taken into account, a revised form of the expression (10) is given by:

$$B_e = \frac{1}{2}(5B_0 - B_{100} - B_{001} - B_{02^00}) + 3\gamma_{22}. \tag{11}$$

Thus, the $B_e$ and $I_e$ values for the molecules of the normal and $^{34}S$ species are calculated to be:

$$B_e = 6099.22_5 \text{ Mc/sec, and}$$
$$I_e = 82.8844_6 \text{ amuÅ}^2 \text{ for } {}^{16}O^{12}C^{32}S,$$

and

$$B_e = 5950.01_7 \text{ Mc/sec, and}$$
$$I_e = 84.9629_5 \text{ amuÅ}^2 \text{ for } {}^{16}O^{12}C^{34}S.$$

TABLE 7. MOLECULAR STRUCTURE OF OCS

| | Bond length (Å) | | |
|---|---|---|---|
| | C–O | C–S | O–S |
| $r_o$ [a] | 1.161 | 1.561 | 2.722 |
| $r_s$ [b] | 1.1602 | 1.5601 | 2.7203 |
| $r_e$ [c] | 1.16 | 1.56 | |
| $r_e$ | $1.157_2$<br>±0.002 | $1.560_6$<br>±0.002 | 2.7178<br>±0.0005 |

a) Ref. 1.
b) Ref. 2.
c) Obtained by infrared, Ref. 4.

The equilibrium structure, $r_e$, is determined by combining the values of $I_e$ thus obtained. The final results are shown in Table 7, compared with values of the $r_s$ and $r_o$ structures.

**C. *l*-Type Doubling Constants and Harmonic Force Constants.** The $l$-type doubling constant of the linear triatomic molecule is a function of $B_e$, the vibrational frequencies, and the Coriolis coupling constants.[10]

$$q_e = \frac{2B_e^2}{h\omega_2}\left\{1 + 4(\zeta_{12}{}^{(x)})^2\frac{\omega_2{}^2}{\omega_1{}^2 - \omega_2{}^2} + 4(\zeta_{23}{}^{(x)})^2\frac{\omega_2{}^2}{\omega_3{}^2 - \omega_2{}^2}\right\}, \tag{12}$$

where $\zeta_{12}{}^{(x)}$ and $\zeta_{23}{}^{(x)}$ satisfy the sum rule, $(\zeta_{12}{}^{(x)})^2 + (\zeta_{23}{}^{(x)})^2 = 1$. Since the Coriolis coupling constants are closely related to the harmonic force constants, the $l$-type doubling constant is one of the important quantities which are applicable to the determination of the quadratic force constants. Morino and Hirota calculated the harmonic force constants of several triatomic molecules by the use of the observed values of the $l$-type doubling constants.[9] It should be mentioned, however, that Eq. (12) holds only for $q_e$, not for $q_v$. The two quantities are related to each other thus:

$$q_v = q_e + \sum_i q_{vi}\left(v_i + \frac{d_i}{2}\right). \tag{13}$$

As the zero-order $l$-type constant, $q_e$, was not known at that time, they had to use $q_v$ at the $v_2=1$ state in place of $q_e$. The change in the $l$-type doubling constant by molecular vibrations is fairly large; hence, the use of $q_v$ in place of $q_e$ possibly caused a fairly large error in the results.

In order to obtain $q_e$, it is necessary to know the values of $q(01^10)$, $q(03^10)$, $q(11^10)$, and $q(01^11)$. These four values were observed in this study; they are listed in Table 3 for the normal OCS molecule. It should be pointed out, however, that the latter three states couple with each other by the Fermi resonances, and that the $q_v$ constants obtained from the microwave spectrum are those for the states perturbed by the Fermi resonance. It may be shown by an argument similar to that stated above in Scetion B for the $\alpha$'s that there exists a sum rule of:

$$q^*_{v1} + 4q^*_{v2} + q^*_{v3} = q_{v1} + 4q_{v2} + q_{v3}, \qquad (14)$$

where $q^*_{vi}$ denotes the observed value of the constant, and $q_{vi}$, the unperturbed value which is involved in (13). Fortunately, the sum gives the correction from $q(01^10)$ to $q_e$:

$$q_e = q(01^10) - \frac{1}{2}(q^*_{v1} + 4q^*_{v2} + q^*_{v3}) \qquad (15)$$

As $q^*_{v1}$, $q^*_{v2}$, and $q^*_{v3}$ were found to be 0.507, $-0.083$, and 0.103 Mc/sec respectively, $q_e$ was calculated to be 6.210 Mc/sec.

The Coriolis coupling constant, $(\zeta_{12}^{(x)})^2 = 0.0225$, obtained by the use of Eq. (12), combined with the zero-order vibrational frequencies, $\omega_1 = 876.64$ cm$^{-1}$, $\omega_2 = 524.09$ cm$^{-1}$, and $\omega_3 = 2093.64$ cm$^{-1}$, leads to the harmonic force constants for the stretching motions in the expression of the potential function:

$$V = \frac{1}{2}f_R(\Delta R)^2 + \frac{1}{2}f_r(\Delta r)^2 + f_{Rr}(\Delta R)(\Delta r), \qquad (16)$$

where $\Delta R$ denotes the displacement of the C–S distance, and $\Delta r$, that of the O–C distance. The results are compared in Table 8 with those obtained by using the vibrational frequencies of isotopically substituted molecules.[11]

TABLE 8. FORCE CONSTANTS OF OCS FROM $l$-TYPE DOUBLING CONSTANTS (in md/Å)

| From $l$-type doubling | From isotopic shift[a] |
|---|---|
| $f_R$(CS) = 7.84 | 7.44 |
| $f_r$(CO) = 15.21 | 16.14 |
| $f_{Rr}$ = 0.50 | 1.04 |

a) Ref. 11.

## Discussion

If two rotational lines in vibrationally excited states which interact each other by a Fermi resonance have nearly the same frequencies, that is, if their $\alpha$'s are nearly equal, the effect on the rotational constants is negligibly small, even if the interaction is large. This is because the effect of the Fermi resonance appears in the rotational constant as a mixing of the rotational constant. The situation really occurs for the $(20^00)$ and $(00^01)$ states of carbonyl sulfide. The rotational constants, $B^0{}_{200}$ and $B^0{}_{001}$, are nearly equal, as Table 3 shows; therefore, the changes in $B$'s by the Fermi resonance due to the interaction term, $k_{113}q_1{}^2q_3$, must be so small that the neglect of this resonance has no serious influence on the analysis of other resonances or of the equilibrium structure. The conclusion is supported by the fact that the energy separation between these two states is more than 3000 cm$^{-1}$. On the other hand, the resonance between $(02^00)$ and $(00^01)$ brings about an appreciable change in the rotational constants, because their $\alpha$'s have different signs with large magnitudes. The resonance between the (100) and (002) states may be small as long as $k_{133}$ is not extraordinarily large, because the energy separation of these two states is more than 3000 cm$^{-1}$. Therefore, as far as the rotational spectra are concerned, it may be sufficient to take into account only the resonances by $k_{122}$ and by $k_{322}$.

Callomon and Thompson considered a Fermi resonance between $(00^01)$ and $(04^00)$.[3] Really, these two levels are fairly close together, so that it might be expected that the fifth-order potential constant, $k_{22223}$, might contribute an appreciable interaction between these two states. In order to discuss this kind of resonance, we must consider the situation much more generally, not only the situation for the rotational constants, but also that for the vibrational frequencies. Recently Morino and Nakagawa have treated the anharmonic potential constants of OCS by taking into consideration even the Fermi resonances due to $k_{22223}$. A detailed discussion of this will be given in a separate report.[11]

The $l$-type doubling constant, $q_v$, considerably change with the excitation of the molecular vibrations. A theoretical consideration of the changes of $q_v$ by vibrations has been undertaken by Morino and Nakagawa.[12] It is clear that the changes are closely connected with the cubic and quartic potential constants. Therefore, the observed values of the changes in $q_v$ with the excitation of vibrational motions, $q_{v1}$, $q_{v2}$ and $q_{v3}$, will provide other information on the anharmonic potential function of the OCS molecule, although lengthy calculation will be required.

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[11] Y. Morino and T. Nakagawa, to be published.

[12] Y. Morino and T. Nakagawa, *J. Chem. Phys.*, **44**, 841 (1966).