Fourier Transform Spectroscopy of Carbonyl Sulfide from 4800 to 8000 cm$^{-1}$ and New Global Analysis of $^{16}$O$^{12}$C$^{32}$S

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We have measured the FT spectrum of natural OCS from 4800 to 8000 cm$^{-1}$ with a near Doppler resolution and a line-position accuracy between 2 and $8 \times 10^{-4}$ cm$^{-1}$. For the normal isotopic species $^{16}$O$^{12}$C$^{32}$S, 37 vibrational transitions have been analyzed for both frequencies and intensities. We also report six bands of $^{16}$O$^{12}$C$^{34}$S, five bands of $^{16}$O$^{13}$C$^{32}$S, two bands of $^{16}$O$^{12}$C$^{33}$S, and two bands of $^{18}$O$^{12}$C$^{32}$S. Important effective Herman–Wallis terms are explained by the anharmonic resonances between closely spaced states. As those results complete the study of the Fourier transform spectra of natural carbonyl sulfide from 1800 to 8000 cm$^{-1}$, a new global rovibrational analysis of $^{16}$O$^{12}$C$^{32}$S has been performed. We have determined a set of 148 molecular parameters, and a statistical agreement is obtained with all the available experimental data. © 1998 Academic Press

INTRODUCTION

The infrared spectra of carbonyl sulfide have been intensively studied over the years. The most recent investigations were mainly devoted to the 1700–3100 cm$^{-1}$ region, by heterodyne or sideband laser techniques (1–5), and also by classical Fourier transform spectroscopy (6, 7). At higher wavenumbers, the FT spectra from 3700 to 4800 cm$^{-1}$ have been recently published (8).

In this paper, we present the analysis of the FT spectra of OCS from 4800 to 8000 cm$^{-1}$. Except the study of very weak bands observed between 6130 and 6650 cm$^{-1}$, thanks to a sensitive multipass optoacoustic cell used with a color center laser (9), this region has not been investigated since 1970 (10), when the 2400–7000 cm$^{-1}$ domain was studied using a grating spectrometer with a resolution of 0.04 cm$^{-1}$ and a line-position accuracy of about 0.01 cm$^{-1}$. The resolution of our FT spectra is close to the Doppler limit ($\sim 0.01$ cm$^{-1}$ at 6000 cm$^{-1}$), and their accuracy is in the range of $2 \times 10^{-4}$ to $1 \times 10^{-3}$ cm$^{-1}$.

As this work completes the systematic study of the infrared spectra of OCS undertaken a few years ago (7), we will also report a refined global analysis of the main isotopomer $^{16}$O$^{12}$C$^{32}$S.

Although the improvement in the line positions is the main goal of this work, we also present an analysis of the experimental intensities, the first one reported for this region.

EXPERIMENTAL DETAILS

The absorption spectrum of carbon oxysulfide was recorded in the range of 4700–8700 cm$^{-1}$ using the Fourier transform spectrometer Bruker IFS120HR of the University of Brussels. The instrument was fitted with a tungsten lamp, a CaF$_2$ beam splitter, and an InSb detector. It was equipped with a long path White-type absorption cell adjusted for 24 transits (42 m path) and fitted with CaF$_2$ windows. The sample was purchased from Aldrich Chemie (96% stated purity) and used without further purification. A total of seven spectra of OCS were recorded in various ranges and experimental conditions as detailed in Table 1. The spectra were recorded using an iris diameter of 1.15 mm, but 1.5 mm for the last spectrum, and they were all left unapodized. The measurements were performed at room temperature (294 K).

The last two columns of Table 1 give additional information, which was used to determine the intensity of the OCS lines from the measurement of their peak amplitude (see below). It was obtained from simulations of a Voigt-shaped OCS line located in the center of each spectral region, in the pressure and instrumental conditions given. The one before the last column lists the ratio of the Lorentz to the Doppler half-widths of the line, assuming that the pressure broadening parameter is equal to $\gamma_0 = 0.14$ cm$^{-1}$/atm (11). The last column gives the corresponding amplitude (in absorbance) of the nonsaturating line relative to that of a pure Doppler profile. The flattening of the line with increasing pressure and lower resolution is clearly put forward.

The line positions were measured using the program "Spectra", which adjusts a Voigt profile to the observed lines in a least-squares fitting procedure (12). They were calibrated against the 3–0 band of CO (13), which had been added to the OCS sample. The calibration of the 5000-cm$^{-1}$ region was improved using the $10^02–00^0$ and $02^02–00^0$ bands of OCS, of which the wavenumbers were known within about $10^{-4}$ cm$^{-1}$, on the basis of the $10^02–10^00$ and $02^02–02^00$ bands.
measured near 4100 cm\(^{-1}\) \((8)\). The line-position accuracy is estimated to be 2, 3, 5, and \(10 \times 10^{-4}\) cm\(^{-1}\) near 5000, 6000, 7000, and 8000 cm\(^{-1}\), respectively.

The peak-finding procedure also provides the peak amplitude of the lines, that we divide by the \(A_{\text{max}}\) values listed in Table 1 to obtain the peak amplitude of the lines in the pure Doppler case. According to formulas recalled in Ref. \((7)\), absolute intensities could then be derived. A good coherence (within less than 10\%) was observed between intensities deduced from different pressure spectra.

We roughly estimate the accuracy of these intensities to be 30\%. That value includes the uncertainty in the measurement of the experimental parameters (\(~15\%) and the error introduced by the approximation used when correcting the peak amplitude of the lines with \(A_{\text{max}}\). This latter error essentially originates from the assumed constancy of the ratio \(\gamma_L/\gamma_D\) over each spectral range (Table 1). Because the Doppler half-width was computed at the center of each spectral range, the error introduced was at most 13\%. The pressure broadening parameter \(\gamma_0\) for OCS is known to vary from about 0.15 cm\(^{-1}\)/atm at \(J = 0\) down to 0.10 cm\(^{-1}\)/atm at \(J \sim 60\), with a maximum value of 0.17 cm\(^{-1}\)/atm at \(J \sim 25\) \((11)\). The value used in the present calculations is the mean value over the range of \(J = 0\) to \(\sim 55\), with an uncertainty of about \(\pm 20\%\). Both errors yield an uncertainty of about 24\% on the ratio \(\gamma_L/\gamma_D\). Finally, because of the \(J\) dependency of the approximated quantities, the corrected line intensities could exhibit small unexplained \(J\) dependencies, but such effects were not observed.

### OBSERVED SPECTRA

All the observed bands are listed in Table 2: 37 for \(^{16}\text{O}^{12}\text{C}^{32}\text{S}\), 6 for \(^{16}\text{O}^{13}\text{C}^{32}\text{S}\), 5 for \(^{16}\text{O}^{12}\text{C}^{33}\text{S}\), 2 for \(^{16}\text{O}^{12}\text{C}^{34}\text{S}\), and 2 for \(^{18}\text{O}^{12}\text{C}^{32}\text{S}\). Uncertainties of the band centers (one \(\sigma\), given in the last digits) include the calibration uncertainty. The right part of this Table presents the results of the analysis of the line intensities, according to formulas recalled in Ref. \((7)\). In the last column, the relative precision of the parameters \(R^2\) and \(S_{\text{BAND}}\) does not include the 30\% associated with the intensity accuracy. The need for the parameters \(R^1_{\text{RES}}\) or \(R^2_{\text{RES}}\) in the Herman–Wallis factor

\[
F_{\text{RES}}(J') = 1 + R^1_{\text{RES}} J' + R^2_{\text{RES}} J'^2
\]

indicates a sensitive \(J\) dependence of the intensities caused by \(l\)-type or anharmonic resonances, and we will explain those effects in details.

The results of the least-squares fits on the observed bands are reported in Table 3 for \(^{16}\text{O}^{12}\text{C}^{32}\text{S}\) and in Table 4 for the other isotopomers. They are classified according to the energy of the upper state of the transition, some upper states being reached from different lower states. In all cases, the lower state parameters were known with high accuracy and were fixed in the \(L–S\) procedure [those parameters can be found in Table IV of Ref. \((6)\) for \(^{16}\text{O}^{12}\text{C}^{32}\text{S}\), in Table XXI of Ref. \((14)\) for \(^{16}\text{O}^{12}\text{C}^{33}\text{S}\), and in Tables XVII–XIX of Ref. \((15)\) for the other isotopomers]. In the 5000–8000 cm\(^{-1}\) range, most states are perturbed, and the convergence of the power series in \(J(J + 1)\) is poor. Because those perturbations are well reproduced in our global analyses, we fix to their predicted values the high-order terms of the \(J(J + 1)\) expansion, and we adjust the lowest-order terms to fit the experimental data. In most cases, the first two terms in the \(J(J + 1)\) power series were let free, improving the \(E_u\) and \(B_v\) parameters. In some cases, mainly for bands observed up to high \(J\) values, the \(D_v\) parameter was also improved. In a few cases, the agreement was perfect by adjusting only the vibrational energy. Uncertainties (one \(\sigma\)) on the vibrational energies do not include the calibration uncertainties which are estimated in the section about the experimental conditions.

For a few strongly perturbed states, the least-squares fit was not possible because the \(J(J + 1)\) expansion is no longer appropriate to describe the rovibrational energies. In such cases (states with a mark \(\ast\) in Tables 2 and 3), the band analysis was limited to low \(J\) values, but the experimental frequencies have been directly introduced in the corresponding global analysis.
The same procedure was applied to states observed in a too limited range of \( J \) values.

Figure 1 presents the vibrational states of the 6\( \nu_1 \) polyad. We will frequently refer to this figure to illustrate their relative position in energy and to explain how they are in interaction through the anharmonic resonances.

### TABLE 2

<table>
<thead>
<tr>
<th>Band</th>
<th>Center (cm(^{-1}))</th>
<th>Band</th>
<th>Num</th>
<th>( J_{\text{min}} )</th>
<th>( J_{\text{max}} )</th>
<th>( R_0^2 ) (10(^{-1}))</th>
<th>( R_0^4 ) (10(^{1}))</th>
<th>( R_0^6 ) (10(^{-1}))</th>
<th>Sano (cm(^2)atm(^{-1}))</th>
<th>Rel. Prec.</th>
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<td>160119732S</td>
<td>4593.2790(2) ( \pm 2 )</td>
<td>1.20 ( \pm 0 ) ( \pm 0 ) ( \pm 0 )</td>
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<td>0</td>
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<td>0.266090</td>
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<td>0</td>
<td>3.14(32)</td>
<td>0.011854</td>
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<td>4587.79(3)</td>
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<td>1.71(58)</td>
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<td>2</td>
<td>65</td>
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<td>0</td>
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<td>64</td>
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\[ \text{Relative Prec.} = \frac{\text{Experimental Error}}{\text{Calculated Value}} \]

Note. A mark * indicates a band for which the least-squares fit was not applicable (too strongly perturbed state, or too few observed lines).

### BAND BY BAND ANALYSIS

**The 10^6 and 14^61 Bands near 4950 cm\(^{-1}\)**

The 10^6–00^60 band is the strongest band in the studied region. The 14^61 state is only 16.5 cm\(^{-1}\) above the 10^62 state, and those states are in relatively strong anharmonic resonance,
directly through the $k_{2223}$ term and indirectly through the $k_{113}$, $k_{122}$, and $k_{1223}$ terms. This interaction yields large high-order terms in the $J(J+1)$ expansion (Table 3).

Another consequence of the heavy mixing of those states is an intensity transfer from the strong $100\ 2-00\ 0\ 0$ band to the very weak $14\ 0\ 1-00\ 0\ 0$ band, which is observed about 20 times as weak as the main band at low $J$ values. At higher $J$ values, the energy difference increases, and reaches about 28 cm$^{-1}$ at $J = 567$, so that the intensity borrowing is reduced from 5 to about 1%. For the weak band, this effect is roughly reproduced by a large and

<table>
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<tr>
<th>UPPER STATE</th>
<th>LOWER STATE</th>
<th>$E_v$ (cm$^{-1}$)</th>
<th>$B$ (10$^{-4}$ cm$^{-1}$)</th>
<th>$D$ (10$^{-7}$ cm$^{-1}$)</th>
<th>$H$ (10$^{-10}$ cm$^{-1}$)</th>
<th>$L$ (cm$^{-1}$)</th>
<th>$M$ (cm$^{-1}$)</th>
<th>$N$ (cm$^{-1}$)</th>
<th>$O$ (cm$^{-1}$)</th>
<th>$P$ (cm$^{-1}$)</th>
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<td>1 0 2 0</td>
<td>0 0 0 0</td>
<td>5932.9675</td>
<td>1.092</td>
<td>1.060</td>
<td>7.380</td>
<td>0.004</td>
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<td>0.004</td>
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Note. Uncertainties (one $\sigma$) are written under the parameters which have been improved in our fits.
negative $R^1$ term in Table 2, whereas a small positive $R^2$ term is observed for the strong band.

Amongst the associated hot bands, a similar but stronger intensity transfer is observed from the 20 0 2–10 0 0 band to the 24 0 1–10 0 0 band. This transfer increases with $J$, and the opposite $J$ dependence of the intensities appears in the $R^2$ terms. Because those upper states are also observed from the ground state near 5800 cm$^{-1}$, their interaction will be discussed later.

A small local perturbation is observed in the 10 0 2–00 0 0 band, because of an anticrossing of the 10 0 2 and 14 4e 1 states near $J = 44$. At $J = 43$, 44, and 45, the observed shifts are $12$, $27$, and $93$ cm$^{-1}$, respectively, clearly visible in the spectrum of which the dispersion is about $43$ cm$^{-1}$. At $J = 44$, the $-0.4\%$ intensity transfer allows us to observe the satellite $R(43)$ line of the 14 4e 1–00 0 0 band at 4966.0914 cm$^{-1}$. This local perturbation is well fitted in our global analysis, because we consider simultaneously the direct and indirect anharmonic interactions between the 100 2 and 14 0 1 states, and the rotational $l$-type resonances between the 14 0 1, 14 2e 1, and 14 4e 1 states. For $^{16}$O$^{12}$C$^{33}$S and $^{16}$O$^{12}$C$^{34}$S, the same anticrossing of the 10 0 2 and 14 4e 1 states is observed, at $J = 47–48$ and $J = 49–50$, respectively.

The 02 0 2 and 06 0 1 Bands near 5150 cm$^{-1}$

The 02 0 2–00 0 0 band is about 17 times as weak as the 10 0 2–00 0 0 band. The hot bands from $\nu_2$ and 2$\nu_2$ states are

### Table 4

Upper States Parameters of Assigned Bands of the Isotopomers of OCS, According to the Expansion into Power Series of $J(J + 1)$ up to the Eighth Order

<table>
<thead>
<tr>
<th>UPPER STATE</th>
<th>LOWER STATE</th>
<th>$E_u$ (cm$^{-1}$)</th>
<th>$B$ (10$^{-4}$ cm$^{-1}$)</th>
<th>$D$ (10$^{-6}$ cm$^{-1}$)</th>
<th>$H$ (10$^{-8}$ cm$^{-1}$)</th>
<th>$L$ (cm)</th>
<th>$M$ (cm)</th>
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Note. Uncertainties (one $\sigma$) are written under the parameters which have been improved in our fits.

### FIG. 1

$\Sigma$ states of the 6$\nu_1$ polyad of OCS, with the anharmonic resonances which are treated as off-diagonal terms in the global rovibrational analysis.
observed thanks to advantageous vibrational factors $F_v$’s for this $\Delta v_2 = 2$ transition, whereas the hot band from $v_1$ is too weak to be observed. The 06$^0$1–00$^0$0 band is observed thanks to a 2% intensity transfer from the 02$^0$2–00$^0$0 band, because the energy difference between 06$^0$1 and 02$^0$2 states is about 75 cm$^{-1}$.

The 00$^0$3–10$^0$0 Band near 5250 cm$^{-1}$

This difference band is very weak and well isolated. At $J' = 30$, we observe the local perturbation caused by the crossing of the 00$^0$3 and 11$^0$0,0 states, but we will discuss this interaction in the 00$^0$3–00$^0$0 band.

The 40$^0$1 and 32$^0$1 Bands near 5450 and 5600 cm$^{-1}$, Respectively

Those two bands are too weak to observe any associated hot or isotopomer band. The 32$^0$1 state crosses the 36$^4$0 state between $J = 9$ and $J = 10$, but their indirect interaction occurs at too low $J$ values to yield an observable local perturbation.

The 20$^0$2 and 24$^1$1 Bands near 5800 cm$^{-1}$

The 20$^0$2–00$^0$0 band is of medium intensity, so that we also observe its first two hot bands, and the OCS$^{34}$S band. The associated 24$^1$1–00$^0$0 band is easily observed because the 20$^0$2 and 24$^1$1 states are very close to each other (Fig. 1). As shown in Fig. 2, those states cross each other near $J = 53$, and their interaction is made more complex by the 24$^2$1 state, with an anticrossing near $J = 63$. From the first anticrossing, we deduce an effective coupling energy of about 2.9 cm$^{-1}$ between the two $\Sigma$ states, resulting, as shown in Fig. 1, from the direct term associated with $k_{22223}$ ($\sim 1.6$ cm$^{-1}$) and from indirect coupling through the $k_{122}$, $k_{113}$, and $k_{1223}$ terms. The 24$^1$1 and 24$^2$1 states are coupled through the rotational $l$-type resonance. This situation is similar to the interaction of the 20$^0$1, 24$^0$0, 24$^2$0, and 24$^4$0 states in the 4$v_1$ polyad (7, 8).

The intensity parameters reported for those two bands in Table 2 are effective parameters, with large and opposite $R_{2RES}$ terms, which give an approximate fitting of the observed values in a limited range of $J$. However, in this particular case a more global analysis of intensities has been performed on the basis of eigenvectors determined in the frequency analysis of the polyad, as we did for the 20$^0$1 state (9). We are concerned with the 20$^0$2, 24$^0$1, and 24$^2$1 states (a, b, and c series, respectively, in Fig. 2). The mixing of those states with each other and with other states of the polyad varies according to $J$ in a complex way. The main eigenvector coefficients of the 20$^0$2, 24$^0$1, and 24$^2$1 states are given in Figs. 3, 4, and 5, respectively. Using the notation $\mu(20^02) = R_v(20^02 \leftarrow 00^00)$ for the vibrational part of the transition dipole moment, with a zero superscript for unperturbed values, the effective dipole moment for a transition to state $i$ receives contributions from all other states of the polyad according to the relation

$$\mu(i) = \sum_j C_{ij} \mu^0(j).$$

This sum can be reduced to a few terms on the basis of the value of the eigenvector coefficients $C_{ij}$ given in Figs. 3–5, and of the unperturbed transition moments $\mu^0(j)$ which are ex-

![FIG. 2. Reduced energies of OCS states between 5788 and 5803 cm$^{-1}$ according to the global analysis. Marks correspond to observed levels.](image)

![FIG. 3. Some eigenvector coefficients of the 20$^0$2 state of OCS (corresponding to the a series of Fig. 2).](image)
expected to rapidly decrease with the number of changes of vibrational quantum numbers

\[ \mu^0(00') \gg \mu^0(20') \gg \mu^0(12') = \mu^0(40') \gg \cdots. \]

This fact is suggested in Fig. 1 by the weight of the lines corresponding to the states of the polyad. So we have to consider the contribution from the $3^2$ band to the intensities of our group of bands. We have found that the intensities of the $00'3, 20'2, 24'01, 24'2e1,$ and $12'2$ bands could be reproduced by using only the first three transition dipole moments listed above. On the basis of the experimental $R^2 F(J)$ at $J = 0$, we use the next three relations

\[
\begin{align*}
\mu(00') &= +0.9708 \mu(00'3) - 0.1352 \mu(20') \\
+ &0.0280 \mu(12') = +(1.437 \times 10^{-6})^{1/2} D \\
\mu(20') &= +0.1059 \mu(00'3) + 0.8526 \mu(20') \\
+ &0.3242 \mu(12') = +(0.213 \times 10^{-6})^{1/2} D \\
\mu(12') &= -0.1196 \mu(00'3) - 0.2291 \mu(20') \\
+ &0.8686 \mu(12') = -(0.076 \times 10^{-6})^{1/2} D
\end{align*}
\]

to deduce the unperturbed transition dipole moments:

\[
\begin{align*}
\mu^0(00'3) &= +1.29 \times 10^{-3} D, \\
\mu^0(20') &= +3.95 \times 10^{-3} D, \quad \text{and} \\
\mu^0(12') &= -3.59 \times 10^{-3} D.
\end{align*}
\]

We now have to consider the $J$ dependence of intensities, which results from the changes of the eigenvector coefficients in the previous equations. For the transitions from the ground state to the $20'2, 24'1,$ and $24'2$ states (series of levels marked with letters a, b, and c, respectively, in Fig. 2), we compare in Fig. 6 the experimental $R^2 F(J)$ values (marks) and the corresponding calculated values (curves) using the unperturbed tran-

\[
\begin{align*}
(R^2 F(J) - 10^{-5} \text{ (Debye)}^2)
\end{align*}
\]

FIG. 4. Some eigenvector coefficients of the $24^11$ state of OCS (corresponding to the a series of Fig. 2).

FIG. 5. Some eigenvector coefficients of the $24^21$ state of OCS (corresponding to the c series of Fig. 2).

FIG. 6. Experimental values of $R^2 F(J)$ for the series of lines which, at $J = 0$, correspond to the $20'2$–$00'0$, $24'1$–$00'0$, and $24'2$–$00'0$ bands of OCS, with annotations a, b, and c, respectively, like in Fig. 2. Continuous curves correspond to calculated values according to the analysis explained in the text. Positive and negative $J$ values correspond to transitions to the $J'$ level in the $R$ and $P$ branch, respectively.
The 12^3\_2 Band near 5950 cm\(^{-1}\)

This weak band is about 20 times as weak as the 3\(\nu_3\) band, and we also observe its first hot band. On the basis of the unperturbed transition dipole moments previously determined, an intensity ratio of 1300 should be expected without intensity transfer from the 3\(\nu_3\) and 2\(\nu_1 + 2\nu_3\) bands.

The 00^3\_3 and 04^3\_2 Bands near 6100 cm\(^{-1}\)

The 00^3\_3–00^0\_0 band is the strongest band of OCS above 5000 cm\(^{-1}\), and many associated hot bands and isotopomer bands are also reported. An ~2% intensity transfer allows us to observe the 04^3\_2–00^0\_0 band. As the energy difference between the 04^3\_2 and 00^3\_3 states increases with \(J\), the intensity borrowing decreases with \(J\), which explains the large and negative \(R^\mathrm{RES}_1\) Herman–Wallis term for this band. The observation is limited to \(J = 65\), whereas Ch. Hornberger (9) reached \(J = 93\) thanks to the high sensitivity of his optoacoustic detection. He also reports the first two hot bands, which were not observed in our spectra. On the other hand, our accuracy is one order of magnitude better, which illustrates the complementarity of both techniques.

A nice perturbation is observed at \(J = 30\) in both branches of the 00^3\_3–00^0\_0 band, as illustrated in Fig. 7. This local perturbation, first reported by Saksena et al. (16), is caused by the 1,10^0\_0 state which crosses the 00^3\_3 state almost exactly at \(J = 30\), so that the \(R(29)\) and \(P(31)\) lines appear as doublets. Figure 8 shows that the 00^3\_3 state is also perturbed by the 1,10^2\_0 state at \(J = 40–41\), and by the 1,10^4\_0 state near \(J = 59\).

According to Fig. 1, the interaction of the 00^3\_3 and 1,10^0\_0 states does not result from a direct 12th-order anharmonic coupling, but from an indirect coupling through the first-, second-, and third-order anharmonic resonances. The interaction with the \(\Delta^e\) and \(\Gamma^e\) states is allowed by the rotational \(l\)-type
The 30^0 2 Band near 6640 cm\(^{-1}\)

This weak band, observed up to \(J^\prime = 54\), was previously measured by Ch. Hornberger \((9)\) up to \(J^\prime = 93\), but with a lower accuracy. According to Fig. 4 of this reference, the 30^0 2 state crosses the 38^4 0 state near \(J = 12\) (with no visible interaction), and is strongly perturbed by the 34^0 1 state at high \(J\) values.

The 22^0 2 Band near 6800 cm\(^{-1}\)

The 22^0 2–00^0 0 band is very weak, and its strongest lines do not exceed 4% absorption in the highest pressure spectrum. The 22^0 2 state is crossed by the 09^4 0 state near \(J = 26\), but the Coriolis interaction between states of so different quantum numbers is too weak to give any observable effect.

The 10^3 and 14^0 2 Bands near 6970 cm\(^{-1}\)

The energy difference between the 10^3 and 14^0 2 states is equal to 14.8 cm\(^{-1}\) at \(J = 0\), but the separation increases with \(J\). For this reason, the intensity transfer from the 10^0 3–00^0 0 band to the 14^0 2–00^0 0 band, which is about 10% at low \(J\) values, rapidly decreases with \(J\), which explains the \(R^\text{RES}\) term for this last band. We have also observed the first hot band from \(\nu_2\).

The 02^3, 40^0 2, and 20^3 2 Bands near 7120, 7470, and 7810 cm\(^{-1}\), Respectively

Those very weak bands are reported for the first time, but the 40^0 2 state was previously observed from the 10^0 0 state \((9)\).

The state is perturbed by the 90^0 0 state, of which the vibrational energy is about 4 cm\(^{-1}\) higher, but this energy difference decreases with \(J\), and the two states cross each other near \(J = 57\). Because the interacting states belong to different polyads in the model of our global analysis, their interaction is not taken into account, so that the calculated values correspond to unperturbed values. The deduced shifts \(-0.0247, -0.0275,\) and \(-0.0327\) cm\(^{-1}\) at \(J = 5, 19,\) and 29, respectively, are reproduced within 0.0005 cm\(^{-1}\) if we consider an effective interaction energy \(W = 0.32 \pm 0.02\) cm\(^{-1}\). This value seems to be compatible with the numerous interaction schemes, of which we suggest a few examples:

\[
40^0 2 \leftrightarrow k_{1113} \rightarrow 70^0 1 \leftrightarrow k_{111} \rightarrow 90^0 0
\]

\[
40^0 2 \leftrightarrow k_{1113} \rightarrow 60^0 1 \leftrightarrow k_{111} \rightarrow 90^0 0
\]

\[
40^0 2 \leftrightarrow k_{113} \rightarrow 60^0 1 \leftrightarrow k_{111} \rightarrow 70^0 1 \leftrightarrow k_{113} \rightarrow 90^0 0
\]

\[
40^0 2 \leftrightarrow k_{113} \rightarrow 60^0 1 \leftrightarrow k_{111} \rightarrow 80^0 0 \leftrightarrow k_{111} \rightarrow 90^0 0
\]

The 40^0 2 state also crosses the 0,14^0 0 state between \(J = 26\) and 27, but the interaction term is completely negligible.

**THE GLOBAL ANALYSIS OF \(^{16}\text{O}\)^{12}\text{C}\(^{32}\text{S}\)**

**The Experimental Data**

The reported results complete the study, undertaken a few years ago, of the Fourier transform spectra of natural carbonyl sulfide from 1800 to 8000 cm\(^{-1}\) \((7, 8)\). This work provides numerous and accurate data, mainly for the main isotopomer \(^{16}\text{O}\)^{12}\text{C}\(^{32}\text{S}\), that can be used in its global rovibrational analysis. In such an analysis, first published in 1986 \((17)\) and improved...
in 1991 (18), we consider any data obtained from microwave, (sub-)millimeter wave, RF, infrared (FT), laser, heterodyne, MBER, Stark, and double-resonance spectroscopic techniques. Since 1990, many new FT spectra have been published (6–8; 19–23), with accuracies between 10^{-3} and 10^{-5} cm^{-1}. Heterodyne frequency measurements, previously limited by the Doppler width at \pm 10^{-5} cm^{-1} (l, 24–26), are now performed at sub-Doppler resolution with accuracies around 10^{-6} cm^{-1} (2–4). The application of saturation techniques in a CO laser sideband spectrometer improves the tunability of those measurements (5; 27–28). The same accuracy is achieved with a broadly tunable sideband CO_{2} spectrometer (29). Not so accurate but highly sensitive, the use of a multipass optoacoustic cell with a color-center laser (9) has allowed us to detect very weak bands in the near infrared region. The infrared spectrum of OCS, previously limited to 7000 cm^{-1}, has been extended to the 12 000 cm^{-1} region thanks to a very sensitive laser diode technique (9). In the 12 000–14 000 cm^{-1} domain, a higher sensitivity is now achieved with a CW Ti:Sa laser combined with an optoacoustic cell (30), and preliminary results for the 00^06–00^00, 04^05–00^00, 110^03–00^00, 01^06–01^01, 10^06–00^00, and 02^06–00^00 bands (31) have been used in our analysis.

On the basis of this review, the data on the infrared spectra of OCS are by far more numerous, more accurate, and concern more states than in the previous global analysis. On the other hand, no new measurements have been performed by Stark spectroscopy, and only one paper has been devoted to the pure rotational spectra (32).

The least-squares fit has been applied to 2664 data, 2241 from zero-field measurements, and 423 from Stark measurements. The data are introduced individually, except for the infrared bands which are observed in a broad range of J values. In those cases, we use, at selected J values, the frequencies calculated in the band fit. Each data receives a weight inversely proportional to the square of its experimental uncertainty.

The Rovibrational Energy Matrix

For each J value of interest, we construct energy matrices, where all the off-diagonal terms of our Hamiltonian are taken into account simultaneously. For zero-field measurements, we consider the rotational l-type resonance, and some anharmonic terms that are explicitly treated because they concern closely spaced levels (the terms associated with k_{122}, k_{1113}, k_{1223}, and k_{22222}). This limited choice preserves the factorization of the energy matrix in submatrices corresponding to the different polyads. For the measurements with an electrical field, we further consider the Stark and the anisotropy of polarizability terms.

Formulas for the diagonal and off-diagonal terms are given in Ref. (17), (18), and (33). We use the same model as in the previous global fit (18), except for the terms which are off-diagonal both in v and in l.
frequency, with reduced deviations $\sim 1.0 - 2.0$. We think that those deviations indicate that our model is not accurate enough for so highly excited vibrational states. We will come back to this point in the next paragraph.

The Molecular Parameters

The quantity and the quality of the now available experimental data allows us to determine more parameters than previously. In 1986 (17), 77 parameters were used in the first global fit (66 zero-field and 11 Stark parameters). In 1991 (18), 91 parameters (78 + 13) were needed. Our weighted least-squares fit now determines 149 parameters (135 + 14). We list in Table 5 those molecular parameters of $^{16}$O$^{12}$C$^{32}$S, respectively referring to the ground state (using power series in the $v_j$'s) and to the equilibrium [using power series in the $(v_j + d/2)$'s], according to the notations explained in Table VIII of Ref. (18). The new parameters essentially are the fourth-order anharmonicity constants ($z_{ijkl}$), the cubic dependence ($\epsilon_{ijkl}$) of the rotational constant, the quadratic dependence ($\beta_{ij}$) of the centrifugal distortion constant, the quadratic dependence ($\mu_{i}$) of the anharmonic resonance associated with $k_{1113}$, and the linear dependence ($v_i$) of the anharmonic resonance associated with $k_{1223}$. The $q_{ij}$ parameter is fixed to the value deduced from $q_{ij}$ according to Ref. (55). It is well known that, in a polynomial fit, the correlation between the parameters increases with the order of the terms. As an example, in the fit of rovibrational energies according to $\langle v_1, v_2, v_3 | k_{1113} q_{ijkl} | v_1 - 3, v_2, v_3 + 1 \rangle$

$= \frac{1}{2} k_{1113} [v_1(v_1 - 1)(v_1 - 2)(v_3 + 1)]^{1/2}$

gives an interaction energy of 14.25 cm$^{-1}$ and, with a 494 cm$^{-1}$ separation, a shift of 0.41 cm$^{-1}$. Because we do not consider this term explicitly as an off-diagonal term, this effect yields important contributions to many high-order diagonal terms of the vibrational energy, which explains the abnormal values obtained for the $z_{ijkl}$ coefficients with one and three indexes. Furthermore, the convergence of the power series in the $v_i$'s is reduced, and higher-order terms should be introduced to reproduce the energies of the highly excited vibrational states.

Another confirmation of the importance of this $k_{1113}$ interaction is given by the analysis of the previously described perturbation of the 40$^0$ state by the 90$^0$ state. The suggested interaction scheme through the $k_{113}$ and $k_{1113}$ terms is compatible with the effective interaction energy of 0.32 cm$^{-1}$.

The agreement is good between the $k_{122}$ parameter we obtain [41.837(1) cm$^{-1}$] and the $ab\ initio$ calculated value 40.791 cm$^{-1}$ of Martin et al. (37), which confirms the few percent accuracy of such predictions. Because the $k_{131}$ parameter is highly correlated with many diagonal parameters (17) and so not well determined in our analysis, we decided 1 year ago to fix it at its $ab\ initio$ value of $-45.891$ cm$^{-1}$ (37). The fit was not so good, with an estimated standard deviation $\sigma = 1.47$, and reduced deviations between 4.0 and 9.0 for states like 22$^2$1, 24$^1$1, 22$^2$2, 10$^3$3, 20$^0$3, and 30$^0$2. Again let free, the $k_{113}$ coefficient has moved to the value of $-30.35(6)$ cm$^{-1}$, whereas the agreement was improved according to the reported final analysis. We think that the deficiencies of our model (mainly the missing $k_{1113}$ off-diagonal term) are partly compensated by many other diagonal and off-diagonal parameters, and in particular the $k_{113}$ term. It is important to keep in mind that we use an effective Hamiltonian, with as few terms as possible, of which the main interest is the (almost) perfect fitting of all experimental data, with a high coherence, and with possible accurate predictions of any not yet observed state. Such predictions can be obtained from one of the authors (A.F.).

CONCLUSIONS

We have completed with this work the systematic study of the FT infrared spectra of natural carbonyl sulfide undertaken a few years ago. To the wavenumber measurements, we have added intensity measurements which are not quite accurate, but which
### Table 5

Molecular Parameters of $^{30}O^{12}C^{32}S$, Respectively, Referring to the Ground State and to the Equilibrium

<table>
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<td>$\gamma_{2}$</td>
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</tr>
<tr>
<td>$\gamma_{3}$</td>
<td>Constant</td>
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</tbody>
</table>

Note: Standard deviations are written under the parameter values (zero for the fixed parameter $q_{11}$). All values are in cm$^{-1}$ but the Stark $m$'s which are in Debye and the polarizability $a$'s which are in cubed centimeters.
concern the whole spectrum, including the hot bands. We have shown that their analysis requires the use of the eigenvector coefficients, particularly when the heavy mixing of interacting states induces sensitive \( J \) dependences of those intensities.

The new global analysis of the main isotopomer \( ^{16}\text{O}^{12}\text{C}^{32}\text{S} \) remains quite good, although the used model could be improved by introducing explicitly more off-diagonal terms, mainly the second-order anharmonic resonance associated with \( k_{1113} \). This global analysis will be a good basis for the study of the other isotopomers of OCS, for which new investigations have been recently undertaken (38) using isotopic enriched products.

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