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High-resolution synchrotron infrared spectroscopy of thiophosgene: The ν_2 and ν_4 fundamental bands near 500 cm^{-1}

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ABSTRACT

Thiophosgene (Cl_2CS) is a favorite model system for studies of photophysics, vibrational dynamics, and intersystem interaction effects. But there are no previous rotationally-resolved infrared studies because the spectra are very congested due to hot bands and multiple isotopic species. This paper reports a detailed study of the ν_2 ($\sim 504\text{ cm}^{-1}$) and ν_4 ($\sim 471\text{ cm}^{-1}$) fundamental bands for the two most abundant isotopomers, $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$, based on spectra with observed line widths of $\sim 0.0008\text{ cm}^{-1}$ obtained at the Canadian Light Source far-infrared beamline using synchrotron radiation and a Bruker IFS125 Fourier transform spectrometer.

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1. Introduction

Thanks in part to its rich electronic spectrum in the visible region, the thiophosgene molecule is a favorite model system for studies of photophysics, vibrational dynamics, and intersystem interactions [1–3]. Many hundreds of vibrational levels in the ground and excited electronic states have been experimentally observed, allowing the development of detailed anharmonic force fields including all six vibrational modes [4–6]. Interestingly, however, there have been no previous systematic high resolution studies of this molecule's vibration–rotation spectrum. The main reason for this omission is that these infrared spectra are highly congested, requiring very high spectral resolution for successful analysis. Congestion arises partly because this is a relatively heavy molecule, with correspondingly small rotational constants ($A \approx 0.119$, $B \approx 0.116$, $C \approx 0.058\text{ cm}^{-1}$), and because there are two low-lying ($\sim 300\text{ cm}^{-1}$) vibrational states giving rise to hot bands in the spectrum. Another significant factor is the presence of multiple isotopic species (from combinations of ^{35}Cl , ^{37}Cl , ^{32}S , ^{34}S , ^{12}C , ^{13}C , etc.). Indeed, the ground vibrational state of the most abundant species ($^{35}\text{Cl}_2^{12}\text{C}^{32}\text{S}$) represents less than 33% of the population at room temperature, and the next most abundant ($^{35}\text{Cl}^{37}\text{Cl}^{12}\text{C}^{32}\text{S}$) less than 22%. The remaining 45% of the population is made up of the other isotopomers and/or excited vibrations, none with more than 8% of the total. The ground state of the third

most abundant isotopomer ($^{37}\text{Cl}_2^{12}\text{C}^{32}\text{S}$) comprises only about 3.5% of the population.

In the present paper, we report a line-by-line analysis of the ν_2 and ν_4 fundamental bands for the two most abundant isotopomers of thiophosgene, based on spectra obtained using synchrotron radiation at the Canadian Light Source (CLS) far-infrared beamline. Previous infrared studies of gas-phase thiophosgene at low and medium resolution were made by Lowell and Jones [7], Downs [8], Brand et al. [9], and Hopper et al. [10]. The correct assignment of the six fundamental vibrational modes in the ground electronic state was established in 1970 by Frenzel et al. [11]. But as mentioned above, the overwhelming majority of spectroscopic work on this molecule has involved its electronic spectra. The bands studied here are: ν_2 (symmetric C–Cl stretch, $\sim 504\text{ cm}^{-1}$) and ν_4 (out-of-plane bend, $\sim 471\text{ cm}^{-1}$). The remaining modes are: ν_1 (S–C stretch, $\sim 1135\text{ cm}^{-1}$); ν_3 (symmetric in-plane bend, $\sim 292\text{ cm}^{-1}$); ν_5 (asymmetric C–Cl stretch, $\sim 813\text{ cm}^{-1}$); and ν_6 (asymmetric in-plane bend, $\sim 310\text{ cm}^{-1}$).

Thiophosgene is an interesting example of a planar molecule which is an “accidentally” near-symmetric oblate rotor, with $A \approx B \approx 2C$. Indeed, it is so close to being a symmetric top that its axes switch with chlorine isotopic substitution: the C_{2v} symmetry axis coincides with the a inertial axis for $^{35}\text{Cl}_2\text{CS}$, but with the b axis for $^{37}\text{Cl}_2\text{CS}$. The ground state microwave spectra of four isotopomers of thiophosgene were extensively studied in 1975 by Carpenter et al. [12]. But even with the availability of this detailed ground state information, a true line-by-line analysis of the infrared spectrum requires (at least!) the full spectral resolution achieved here, where we observe line widths of about 0.0008 cm^{-1} (unapodized).

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2. Experimental details

Traditionally, most infrared applications of synchrotron radiation have involved condensed-phase studies with low or medium spectral resolution and high spatial resolution, in particular spectromicroscopy of biological samples. More recently there have been promising demonstrations that the brightness of synchrotron sources is useful for gas-phase studies with high spectral resolution, particularly in the far-infrared region [13–16]. At the CLS, the far-infrared beamline has already been used for detailed studies of a number of molecules, including acrolein [17–19], thiophene [20], pyrrole [21], β -propiolactone [22], methyl silane [23], and methanol [24]. The excellent spectral resolution achieved in these studies (often $<0.001\text{ cm}^{-1}$) is of course a function of the spectrometer, not the synchrotron. But it is brightness of the synchrotron source which allows high-resolution spectra to be recorded with a good signal-to-noise ratio in a reasonable time.

The spectra used for the present analysis were recorded using the CLS Bruker IFS 125HR Fourier transform spectrometer, fitted with a KBr beamsplitter and a liquid-helium cooled Ge:Cu detector. It was operated with its full spectral resolution, as given by a 9.4 m maximum optical path difference. The 2 m multiple-traversal cell [25] was set for a total absorption path of 40 m. One spectrum, used for the ν_2 band analysis, was taken at a temperature of 282 K with a Cl_2CS sample pressure of 0.02 Torr. A second spectrum, used for the weaker ν_4 band, was taken at room temperature (295 K) with a pressure of 0.20 Torr. They were averages of 143 or 288 double (forward and back) interferometer scans recorded at a fringe rate of 40 kHz, giving total data acquisition times of about 15 or 30 h, respectively, for the 0.02 and 0.20 Torr spectra. Wavenumber calibration was made using lines due to traces of water vapor present in the cell, with standard line positions taken from Horneman et al. [26]. This resulted in corrections of -0.0003 and -0.0004 cm^{-1} , respectively, being applied to the raw spectra. The thiophosgene sample was used without any special purification except for several freeze–pump–thaw cycles on the liquid after attachment to the gas manifold. Although dimerization can be a problem with this molecule, our relatively low sample pressures probably minimize such effects.

Some preliminary lower resolution spectra were also recorded at NRC using a Bomem DA8 spectrometer and a 0.3 m absorption cell. One of these is shown in Fig. 1, which is a survey of the region of interest here taken at room temperature with a pressure of 0.2 Torr and a path of 6 m. The stronger sharp features in Fig. 1 are due to water vapor. The ν_2 and ν_4 band origins are indicated

Fig. 1. Survey spectrum of thiophosgene (0.2 Torr, 6 m path) showing the region of the ν_4 and ν_2 fundamental bands. The strong sharp lines are due to water vapor impurity in the sample.

with arrows for the most abundant isotopomer, $^{35}\text{Cl}_2\text{CS}$. Note the weaker c -type ν_4 band with a relatively sharp Q-branch feature, and the much stronger a -type ν_2 band, whose exact center is not so obvious. The vital importance of high resolution for these congested bands is illustrated in Fig. 2, which shows a small and relatively uncrowded section of the ν_2 band. The top trace in Fig. 2 is from the 0.02 Torr CLS spectrum, and the bottom trace from the 0.20 Torr NRC spectrum. In the center trace, the CLS spectrum has been smoothed to match (approximately) the lower resolution of the NRC spectrum. Indeed, the match is good, confirming that the NRC spectrum was accurate. But the heavy overlapping and blending of lines in the NRC spectrum made it virtually impossible to make reliable line-by-line assignments (unless the correct answer was already known or very precisely guessed).

3. Results and analysis

Ground state parameters were fixed at their microwave values [12], and our analysis made extensive use of the simulation and fitting program PGOPHER, developed by C.M. Western [27]. For the abundant isotopomer, $^{35}\text{Cl}_2\text{CS}$, the effect of ^{35}Cl nuclear spin statistics is that ground state rotational levels have statistical weights of 3:5 for $K_a = \text{even:odd}$. The next most abundant form, $^{35}\text{Cl}^{37}\text{ClCS}$, is not symmetric and there is no such effect.

3.1. The ν_2 band

We began with the ν_2 band of the abundant isotope, $^{35}\text{Cl}_2\text{CS}$, which has a -type rotational selection rules: $\Delta K_a = 0$, $\Delta K_c = \pm 1$. Certain ranges in the P - and R -branches of this band show characteristic clusters of lines, as illustrated in Fig. 3, with a spacing between clusters of approximately $2C \approx 0.115\text{ cm}^{-1}$. But these are not simply $P(J)$ and $R(J)$ multiplets with common values of K . Rather, each multiplet has a common value of $(2J - K_c)$. This is explained as follows. Since $A \approx B \approx 2C$ for this molecule, the energy of a given level (J, K_a, K_c) is approximately equal to $C[2J(J+1) - K_c^2]$. Thus the location of a given R -branch transition, relative to the origin, is

Fig. 2. A small section of the ν_2 band of thiophosgene comparing the present high-resolution (0.00096 cm^{-1}) CLS spectrum (top trace) with an earlier lower resolution (0.0022 cm^{-1}) NRC spectrum (bottom trace). The equivalence of these results is confirmed by the middle trace, where the CLS spectrum has been smoothed to match.

Fig. 3. Illustration of the *P*- and *R*-branch clusters (upper and lower traces, respectively) observed in the ν_2 band of $^{35}\text{Cl}_2\text{CS}$. The clusters have a spacing of about $2C$, and consist of components with equal values of $(2J - K_c)$, as indicated.

approximately $2C(2J - K_c)$, and transitions with common values of $(2J - K_c)$ tend to cluster together. The labels in Fig. 3 give the values of $(2J'' - K_c'')$ for each cluster. Within each cluster, the strongest line is the unresolved oblate-limit asymmetry doublet with $K_c = J$, for example,

$$(J, K_a, K_c) = (33, 0, 33) \leftarrow (32, 0, 32) \text{ and } (33, 1, 33) \leftarrow (32, 1, 32),$$

for the *R*-branch line at 501.67 cm^{-1} (Fig. 3). Then the adjacent line in the cluster is a slightly weaker doublet with J reduced by one and K_c reduced by two, for example,

$$(J, K_a, K_c) = (32, 1, 31) \leftarrow (31, 1, 30) \text{ and } (32, 2, 31) \leftarrow (31, 2, 30),$$

and so on.

Our first step in the analysis of this band was the assignment of a few hundred of the stronger lines of these *P*- and *R*-branch clusters. This gave good preliminary values for the upper state parameters $(A' + B')/2$ and C' , but since all of these transitions were unresolved asymmetry doublets, it was not very sensitive to the value of the asymmetry parameter $(A' - B')$. For this type of band, it turns out that the *Q*-branch region is most sensitive to the asymmetry parameter, and here the simulation capability of PGOPHER was particularly useful in discovering the correct answer. We also used the notable “rotational parameter trackbar” feature of the JB95 simulation program [28] at this stage.

Having thus determined initial upper state rotational parameters for the ν_2 band of $^{35}\text{Cl}_2\text{CS}$, we turned to same band of the mixed isotope $^{35}\text{Cl}^{37}\text{ClCS}$, starting with rotational parameters estimated from those of $^{35}\text{Cl}_2\text{CS}$ and an approximate band origin from visual inspection of the spectrum. Fortunately, there are regions where the same *P*- and *R*-branch clusters are clearly visible for $^{35}\text{Cl}^{37}\text{ClCS}$, in spite of the competition from $^{35}\text{Cl}_2\text{CS}$. For example, one good region is around $503.9\text{--}505.0\text{ cm}^{-1}$ where the $^{35}\text{Cl}_2\text{CS}$

R-branch is weak (low J -values), and another is around 493 cm^{-1} where the individual $^{35}\text{Cl}^{37}\text{ClCS}$ clusters are still recognizable but the $^{35}\text{Cl}_2\text{CS}$ clusters have merged into each other. So the assignment of numerous lines of these clusters was not too difficult for $^{35}\text{Cl}^{37}\text{ClCS}$. Note that ν_2 for $^{35}\text{Cl}^{37}\text{ClCS}$ is actually an *a*-, *b*-hybrid band since the molecular “symmetry” axis (the C–S bond axis) has projections on both the *a* and *b* inertial axes. But this makes little difference for the *P*- and *R*-branch regions where unresolved oblate asymmetry doublets dominate the spectrum. Differences are more evident in the *Q*-branch region, where once more we used simulations to refine the value of $(A' - B')$.

With preliminary parameters for both abundant isotopes, we proceeded to assign many more transitions, reaching a total of about 1720 for $^{35}\text{Cl}_2\text{CS}$ ($J' = 9\text{--}84$) and 650 for $^{35}\text{Cl}^{37}\text{ClCS}$ ($J' = 16\text{--}83$). In doing so, we used steadily updated simulations to help choose only those lines which were not too blended. Having a reliable simulation of the generally stronger $^{35}\text{Cl}_2\text{CS}$ transitions was especially useful in selecting only the most favorable (unblended) $^{35}\text{Cl}^{37}\text{ClCS}$ lines to include in the analysis. Fig. 4 shows an example of simulated spectra for the *R*-branch, covering the same region as in Fig. 1. Here the clusters are readily evident for $^{35}\text{Cl}_2\text{CS}$ (with $J \approx 27$), but not for $^{35}\text{Cl}^{37}\text{ClCS}$ (with $J \approx 70$) because its adjacent clusters have merged into one another. Another example is shown in Fig. 5, which covers the *Q*-branch region of $^{35}\text{Cl}_2\text{CS}$. Here the *R*-branch clusters of $^{35}\text{Cl}^{37}\text{ClCS}$ are well defined in the simulation, but not very evident in the observed spectrum because of the competing $^{35}\text{Cl}_2\text{CS}$ *Q*-branch transitions.

3.2. The ν_4 band

The ν_4 band arises from the out-of-plane vibration of thiophosgene and has *c*-type rotational selection rules: $\Delta K_a = \pm 1$, $\Delta K_c = 0$. Distinctive line clusters are also visible for ν_4 , even with medium resolution, but they are more apparent in the *P*-branch than in the *R*-branch because the latter region is somewhat overlapped by the stronger ν_2 band (see Fig. 1). A pair of these ν_4 band *P*-branch clusters is illustrated in Fig. 6. They are separated by approximately $(A + B) \approx 0.233\text{ cm}^{-1}$, an amount which is about twice the spacing of the ν_2 band clusters. Each cluster is a “normal” $P(J)$ or $R(J)$ multiplet whose components have the same value of J but different values of (K_a, K_c) . Since the band origin could be accurately estimated from the *Q*-branch peak position (see Fig. 1), the correct J -numbering of these multiplets was fairly easy to determine. However, the correct K -numbering was more difficult.

Fig. 4. Small portion of the ν_2 band of thiophosgene, showing observed (upper trace) and simulated (lower three traces) spectra in the *R*-branch region. The sum of the $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$ simulations accounts for most of the observed lines. Note this is the same region shown in Fig. 2.

Fig. 5. The region of the $^{35}\text{Cl}_2\text{CS}$ Q-branch of the ν_2 band of thiophosgene, showing observed (upper trace) and simulated (lower three traces) spectra.

Fig. 6. Small portion of the ν_4 band of thiophosgene, showing observed (upper trace) and simulated (lower three traces) spectra in the P-branch region. The simulations of the fundamental bands of $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$ account for most of the observed lines. The remaining observed lines (unaccounted for in the simulated sum) must be due to hot bands and other isotopomers.

The weakest transitions in each cluster are those with the highest values of K_c , each of which is an unresolved asymmetry doublet. These become stronger as K_c decreases (and K_a increases), but at a certain point (which depends on J) the asymmetry doubling becomes significant and the regular pattern of the cluster becomes fragmented. It is around this point that the apparent peak of the cluster is formed. In Fig. 6, where $J \approx 20$, this happens around $K_c \approx 6$. Since the strongest transitions here are those with resolved asymmetry doubling, the P- and R-branch regions for ν_4 are sensitive to the value of $(A - B)$, in contrast to the ν_2 band considered above. This actually made it more difficult to determine the K assignments for the individual cluster components, but it meant that once the correct assignments were made, the analysis could rely primarily on the P-branch without much data from the Q-branch (too congested) and the R-branch (overlapped by ν_2).

As in the case of the ν_2 band, we first obtained initial parameters for $^{35}\text{Cl}_2\text{CS}$, used these to estimate parameters for $^{35}\text{Cl}^{37}\text{ClCS}$, and then extended the assignments for both isotopomers, continually updating the PGOPHER simulation so that it was possible to choose only the “best” lines (i.e. relatively strong, sharp, and unblended) to include in the analysis. Ultimately, we reached a total of about 1125 transitions for $^{35}\text{Cl}_2\text{CS}$ ($J' = 8\text{--}80$) and 780 for $^{35}\text{Cl}^{37}\text{ClCS}$ ($J' = 8\text{--}75$). All were P-branch except for a few $^{35}\text{Cl}_2\text{CS}$ R-branch transitions. The illustration in Fig. 6 shows a relatively

uncrowded region of the P-branch, whereas that in Fig. 7 shows the very congested central Q-branch region. Comparison of the simulations in these figures (which are based on our fitted parameters, see below) with the observed spectra shows that most, but not all, of the observed structure is explained by the fundamental bands of the two most abundant isotopomers. The remaining unexplained structure is due to hot bands and minor isotopomers.

3.3. Analysis

The analyses were carried out in terms of an A-reduced asymmetric rotor Hamiltonian [29]. We used our own asymmetric rotor fitting program [17,30] for convenience in data handling, but the results were essentially identical to those from PGOPHER. The resulting parameters are listed in Table 1 for $^{35}\text{Cl}_2\text{CS}$ and Table 2 for $^{35}\text{Cl}^{37}\text{ClCS}$. The quality of the fits was excellent, as shown by remarkable rms deviations of only 0.000085 and 0.000110 cm^{-1} for $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$, respectively, and by the very small parameter uncertainties in Tables 1 and 2. However, we should be cautious when interpreting this apparently ultra-high precision. For one thing, all ground state parameters were fixed at microwave values [12] in the fits, so the uncertainties in Tables 1 and 2 really apply to the changes of the parameters with respect to their ground state values. Also, as explained above, the lines chosen for inclusion in the fits were deliberately pre-selected to be “good” in the sense of being sharp and unblended. In other words, the results are indeed very precise, but probably not quite as good as implied by the listed parameter uncertainties.

If the ground state parameters were also allowed to vary in the present infrared analysis (fitting ν_2 and ν_4 simultaneously), then the sum of squares of the fit decreased only very slightly ($\sim 1\%$) and the ground state parameter uncertainties increased up to 15 times their quoted microwave values [12]. But these new, less precise, infrared ground state parameters still agreed well with the microwave ones within their respective uncertainties (3σ). (The original microwave data are not readily available for a simultaneous fit.)

Fig. 7. Central region of the Q-branch of the ν_4 band of thiophosgene, showing observed (upper trace) and simulated (lower trace) spectra. The simulation includes transitions up to $J = 105$. It is evident here that the ν_4 band origins can be directly estimated (without an analysis) to within $\approx 0.02 \text{ cm}^{-1}$. The observed spectrum here (and in Fig. 6) is the 0.20 Torr CLS result.

Table 1Molecular parameters for thiophosgene, $^{35}\text{Cl}_2^{12}\text{C}^{32}\text{S}$ (in cm^{-1}).^a

	$\nu_4 = 1$	$\nu_2 = 1$	Ground state ^b
ν_0	471.04267(1)	503.80679(1)	0.0
A	0.118568910(10)	0.118381591(11)	0.118659052(10)
B	0.115571891(10)	0.115474405(17)	0.115550298(10)
C	0.058526954(7)	0.058377607(4)	0.058477122(7)
$10^7 \times \Delta_K$	0.42166(5)	0.44148(12)	0.43353(23)
$10^7 \times \Delta_{JK}$	−0.07794(6)	−0.09685(15)	−0.08940(37)
$10^7 \times \Delta_J$	0.218516(14)	0.217436(41)	0.21708(20)
$10^7 \times \delta_K$	0.180708(16)	0.181206(27)	0.17996(20)
$10^7 \times \delta_J$	0.093359(8)	0.092967(21)	0.09280(7)

^a Quantities in parentheses correspond to 1σ from the respective least-squares fits.^b For the present infrared analysis, the ground state parameters were fixed at these values from Carpenter et al. [12].**Table 2**Molecular parameters for thiophosgene, $^{35}\text{Cl}^{37}\text{Cl}^{12}\text{C}^{32}\text{S}$ (in cm^{-1}).^a

	$\nu_4 = 1$	$\nu_2 = 1$	Ground state ^b
ν_0	470.67287(1)	499.54176(1)	0.0
A	0.116811609(15)	0.116667301(49)	0.116857866(13)
B	0.113097036(18)	0.112978068(55)	0.113121548(10)
C	0.057465306(11)	0.057319518(9)	0.057416517(7)
$10^7 \times \Delta_K$	0.31926(10)	0.3198(7)	0.31702(13)
$10^7 \times \Delta_{JK}$	−0.06643(11)	−0.0714(7)	−0.06371(20)
$10^7 \times \Delta_J$	0.225606(25)	0.22296(16)	0.2219(13)
$10^7 \times \delta_K$	0.201240(33)	0.21020(18)	0.20561(67)
$10^7 \times \delta_J$	0.097174(15)	0.09609(8)	0.09557(3)

^a Quantities in parentheses correspond to 1σ from the respective least-squares fits.^b For the present infrared analysis, the ground state parameters were fixed at these values from Carpenter et al. [12].

There is a Coriolis interaction between the two upper states studied here, $\nu_2 = 1$ and $\nu_4 = 1$. In the simpler case of $^{35}\text{Cl}_2\text{CS}$, it is a purely b -type interaction for which Frenzel et al. [11] estimated the dimensionless zeta parameter to be $\zeta_4 2^b = -0.189$, giving an interaction matrix element of about $2B\zeta = 0.043 \text{ cm}^{-1}$. Including this interaction in the analysis resulted in a marginally (2.5%) better fit in which (as expected) the B' values for ν_2 and ν_4 were highly correlated with the Coriolis parameter. Since the separation of the two states is almost 300 times greater than the largest rotational constant, no significant local resonances were observed which might have served to precisely fix the Coriolis interaction. We believe that the slight improvement provided by the Coriolis fit (which might be due to chance) does not make up for its added complexity, and that the non-Coriolis parameters reported here will be more generally useful.

3.4. Discussion of parameters

The most basic results of the present study are summarized in Table 3, which shows the changes in rotational constants for the two bands studied here, relative to the ground state, in MHz units. The C constant increases upon excitation of the ν_4 mode, which is reasonable if we think of ν_4 as a pure out-of-plane bend with no change in C–S or C–Cl bond lengths. And C decreases with excitation of ν_2 , which is also a reasonable consequence of anharmonicity in the C–Cl bond stretch. These changes in C are just slightly (2%) less for $^{35}\text{Cl}^{37}\text{ClCS}$ than for $^{35}\text{Cl}_2\text{CS}$, as expected. The A and B constants mostly decrease with excitation of ν_4 and ν_2 , except for B of $^{35}\text{Cl}_2\text{CS}$ in ν_4 . In order to compare the two isotopomers, we have to remember that the inertial axes undergo a rotation of about 38°

Table 3Observed changes in rotational parameters for the thiophosgene ν_4 and ν_2 fundamental bands (in MHz).

	ν_4 band		ν_2 band	
	$^{35}\text{Cl}_2\text{CS}$	$^{35}\text{Cl}^{37}\text{ClCS}$	$^{35}\text{Cl}_2\text{CS}$	$^{35}\text{Cl}^{37}\text{ClCS}$
$A' - A''$	−2.702	−1.387	−8.318	−5.713
$B' - B''$	0.647	−0.735	−2.275	−4.301
$C' - C''$	1.494	1.463	−2.983	−2.908

[12] between the two. However, a simple axis rotation does not account very well for the variation between isotopomers. Perhaps there are further differences due to changes in the vibrational motions (particularly ν_2) arising from the change of molecular symmetry from C_{2v} to C_s in going from $^{35}\text{Cl}_2\text{CS}$ to $^{35}\text{Cl}^{37}\text{ClCS}$.

3.5. Other bands

With accurate values for the band origins and changes in rotational parameters of $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$, we are in a good position to estimate such parameters for $^{37}\text{Cl}_2\text{CS}$. The ν_4 Q-branch origin for $^{37}\text{Cl}_2\text{CS}$ is evident in our spectrum just where it would be expected, at about $470.304 \pm 0.02 \text{ cm}^{-1}$. Moreover, we have precise microwave values for the ground state parameters of $^{37}\text{Cl}_2\text{CS}$. So one might expect it to be possible to assign the $^{37}\text{Cl}_2\text{CS}$ spectra and include this isotopomer in the present study. This is unfortunately not the case: the $^{37}\text{Cl}_2\text{CS}$ spectrum is just too weak for us to assign because of its low abundance, which is about 9.4 times smaller than that of $^{35}\text{Cl}_2\text{CS}$.

Indeed, there are four hot bands that should be stronger than the $^{37}\text{Cl}_2\text{CS}$ fundamental band, namely those arising from the $\nu_3 = 1$ ($\sim 292 \text{ cm}^{-1}$) and $\nu_6 = 1$ ($\sim 310 \text{ cm}^{-1}$) states for both $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$. Hot bands were not readily evident in the ν_2 region since this band is crowded and its Q-branch structure is rather diffuse. But in the ν_4 region, we can distinguish a number of additional Q-branch features since these are relatively sharp and distinctive. There is a pair of Q-branches with origins at about 469.64 and 469.29 cm^{-1} . Their separation (0.35 cm^{-1}) is similar to the observed separation (0.37 cm^{-1}) of the $^{35}\text{Cl}_2\text{CS}$ and $^{35}\text{Cl}^{37}\text{ClCS}$ fundamentals, so it is natural to assign them to the same hot band for these two isotopomers. Other hot band Q-branches may be present at about 470.53 , 470.91 , and 471.27 cm^{-1} , but these are increasingly less certain because they overlap with the strong fundamental Q-branches (see Fig. 7). All these apparent hot band Q-branches seem, if anything, to be a bit weaker than would be expected for the ν_3 and $\nu_6 = 1$ states. So it is possible that additional hot band Q-branches are completely “hidden” under those of the fundamentals.

There are also some regularly-spaced series of features observed in the ν_4 region which must be the peaks of hot-band P-branch clusters. One such peak can be seen at 466.175 cm^{-1} in Fig. 6. Intensities in these series are approximately consistent with their assignment to the ν_3 or $\nu_6 = 1$ hot bands. But detailed analysis is not practical at this time because of their relative weakness and because we do not know the rotational parameters for the lower states (ν_3 or $\nu_6 = 1$).

4. Conclusions

In the case of an asymmetric rotor for which ground state parameters are already known and Coriolis resonances and centrifugal distortion are not too important, an infrared analysis essentially involves determination of three relatively small parameters, the vibrational changes in A , B , and C , even for seemingly complex bands like those studied here. Such a three-dimensional search for a solution in (A, B, C) space might seem rather trivial, and indeed

this dimensionality may be closer to two if planarity constraints are invoked. But this triviality was not evident to us in the present work! We found it surprisingly tricky to find the correct answers (Table 3), which in retrospect seem so simple. Part of the problem is that the high resolution band contour can be extremely sensitive to very small changes in the rotational parameters. Even when close to the correct solution, the calculated pattern of lines may not seem to resemble the observed spectrum. Another factor is the limited capacity of humans for large systematic multi-dimensional searches, even with the help of good tools like PGOPHER. We tend to be impatient, easily distracted, and to repeat the same search paths. In this respect, evolutionary algorithm techniques [31] provide an attractive option, since computers are fast, patient, and uncomplaining.

In conclusion, we report here the first high resolution infrared study of thiophosgene, a molecule which is a popular prototype for investigations of photophysics, intersystem interactions, and vibrational relaxation. The ν_2 (symmetric C–Cl stretch) and ν_4 (out-of-plane bend) fundamental bands in the 500 cm^{-1} region have been analyzed for the two most abundant isotopomers, $^{35}\text{Cl}_2^{12}\text{C}^{32}\text{S}$ and $^{35}\text{Cl}^{37}\text{Cl}^{12}\text{C}^{32}\text{S}$. For each of these four bands, some 600–1700 assigned transitions were fitted to obtain accurate upper state rotational and centrifugal distortion parameters. Ground state parameters were fixed at the microwave values of Carpenter et al. [12], which proved to be entirely satisfactory. The establishment of a precise value for the out-of-plane fundamental ν_4 should be helpful for establishing the inversion splittings in the singlet and triplet excited electronic states which determine the barrier heights to molecular inversion. Our future efforts with thiophosgene will focus on the weaker ν_3 and ν_6 bands in the 300 cm^{-1} region.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State Univer-

sity Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm).

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