First far-infrared high resolution analysis of the ν_6 band
of phosgene $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$

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Abstract

A Fourier transform spectrum of phosgene (Cl_2CO) has been recorded in the $22.5\ \mu\text{m}$ spectral region at a resolution of $0.00102\ \text{cm}^{-1}$ using a Bruker IFS125HR spectrometer coupled to synchrotron radiation leading to the observation of the ν_6 vibrational bands of the two isotopologues $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$. The corresponding upper state ro-vibrational levels were fit using Watson-type Hamiltonians. In this way it was possible to reproduce the upper state ro-vibrational levels to within the experimental uncertainty i.e. $\sim 0.30 \times 10^{-3}\ \text{cm}^{-1}$. Very accurate rotational and centrifugal distortion constants were derived from the fit together with the following band centers: $\nu_0(\nu_6, ^{35}\text{Cl}_2\text{CO}) = 443.172062(15)\ \text{cm}^{-1}$, $\nu_0(\nu_6, ^{35}\text{Cl}^{37}\text{ClCO}) = 440.534956(17)\ \text{cm}^{-1}$.

1. Introduction

Phosgene, Cl_2CO , is an asymmetric top molecule and has been the topic of a number of microwave studies [1-5] in which the ground state constants as well as the first excited state constants of its various isotopic species were determined. In the infrared region, however, only two bands, ν_1 and ν_5 of the most abundant isotopic species ($^{35}\text{Cl}_2\text{CO}$) have been partly studied at high resolution using diode laser spectroscopy [4] and, then, studied extensively using FTS spectra using synchrotron radiation from SOLEIL [6] where the corresponding bands of $^{35}\text{Cl}^{37}\text{ClCO}$ were also investigated. This study determined an improved set of ground state rotational constants as well as accurate constants of the upper states of these bands.

This paper presents the first detailed extensive analysis of the ν_6 bands of the two isotopologues $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ in the 445 cm^{-1} region. It has to be noticed that due to the density of the spectrum and the weakness of the ν_6 band of $^{37}\text{Cl}_2\text{CO}$ (Band intensity about 10 times lower than the band intensity of the main isotopologue) it has not been possible to locate it unambiguously. The transition assignments have been extended to very high quantum numbers. This work was done using a high-resolution (0.00102 cm^{-1}) Fourier transform spectrum recorded at a temperature of 197 K. The upper state rotational constants were obtained using a Watson-type Hamiltonian written in the I^r ($x = b$, $y = c$, $z = a$ representation). The phosgene molecule $^{35}\text{Cl}_2\text{CO}$ has C_{2v} symmetry, and its structure as well as its symmetry properties and nuclear spin statistical weights are given in ref. [6]. The C_s point group character table useful for the unsymmetrical isotopic species is given as well in this reference.

2. Experimental details

High-resolution absorption spectrum of phosgene was recorded on the AILES Beamline at Synchrotron SOLEIL using the Synchrotron light source, coupled to the Bruker IFS125HR Fourier transform spectrometer¹ [7, 8] and a newly developed cryogenic multipass cell [9]. The

¹Certain commercial equipment instruments or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

instrument was equipped with 6 μm mylar multilayer beamsplitter. The synchrotron source was operated with 430 mA ring current and a liquid helium cooled Si bolometer detector was used in conjunction with a 50-680 cm^{-1} bandpass optical filter, to improve the S/N ratio and, incidentally, minimize the size of the data files. The spectrometer was evacuated to about 5×10^{-3} Pa in order to minimize H_2O and CO_2 absorptions. The instrument was operated without entrance aperture at the full spectral resolution (0.00102 cm^{-1}) given by the 882.35 cm maximum optical path difference (d_{MOPD}), as defined in the Bruker software ($\text{Resolution} = 0.9/d_{\text{MOPD}}$). The spectrum was recorded with a 60 kHz scanner frequency. The SOLEIL-LISA cryo-cell is fully described elsewhere [9] and only a few relevant details are given here. The cell optical set-up is based on a 1.5 m base length Barskaya-Chernin five-mirrors arrangement [10], providing for maximum vibro-stability. The optical path length can be adjusted in 3 m increments between about 3 and 141 m in the far IR, but longer path lengths can be achieved in the near to mid IR. The mirrors can be retuned at any time and the optical path rechecked with a coaxial laser beam in the visible. In this experiment an optical path of 93.14 m was used. This value takes into account the distance between the surface of the field mirror and the windows of the cell ($2 \times 7 \text{ cm}$). For this experiment, the spectrum was recorded at a regulated temperature of $197 \pm 2 \text{ K}$, along the entire optical path. To limit acoustic noise during data acquisition, only totally vibration-free ionic and cryogenic pumps are in operation.

Triphosgene was purchased from Sigma Aldrich and heated to generate phosgene. Phosgene production begins at a temperature of $80 \text{ }^\circ\text{C}$, below which the gas is not produced. The reaction proceeds cleanly up to $110 \text{ }^\circ\text{C}$ at a steady rate. Before use the sample was purified by freeze-and-thaw cycles to remove any non-condensable impurities. The following procedure was used for measurements: first a background spectrum was recorded at the same temperature of 197 K while the cell was being continuously evacuated; next the infrared gas cell was filled and passivated with Cl_2CO vapor and for the final measurement, a sample pressure of $1.06 \pm 0.2 \text{ hPa}$ was used. The sample pressure in the cell was measured using a home-made cryogenic precision capacitive pressure gauge [11]. The spectrum was ratioed against a single channel background spectrum of the empty cell which was recorded at a resolution of 0.01 cm^{-1} in order to ensure the best possible

signal-to-noise in the ratioed spectrum. For the Fourier transform, a Mertz-phase correction, 4 cm^{-1} phase resolution, a zero-filling factor of 2 and a boxcar apodization function were applied to the averaged interferograms (918 scans). The spectrum was calibrated with residual CO_2 and H_2O lines observed in the spectrum with their wavenumbers taken from HITRAN [12]. The resulting accuracy is $\pm 0.00017\text{ cm}^{-1}$ (RMS) for well isolated lines.

Fig. 1 gives an overview of the phosgene spectrum around $22.5\text{ }\mu\text{m}$ showing the high signal-to-noise ratios which was obtained. The distinctive shapes of the two A-type ν_6 bands with their narrow Q-branches are clearly visible. Also simulations performed using the Hamiltonian constants determined in this work show a very good agreement with the observation.

3. Assignments and results.

The line assignment process proved to be somewhat difficult given the density of lines in the spectrum. Fortunately the low recording temperature (197 K) led to a simplification of the spectrum through the weakening of the various hot bands. The first assignments were performed for the ν_6 of the $^{35}\text{Cl}_2\text{CO}$ species using previous microwave results [5]. Then as soon as a few lines were assigned the corresponding upper state energy levels were fit using Watson-type Hamiltonians (Table 1) [13] and the refined upper state Hamiltonian constants were used to perform more reliable predictions allowing one to assign new lines. The process was repeated until it was no longer possible to locate and assign new lines with confidence. To assign the ν_6 band of the unsymmetrical phosgene $^{35}\text{Cl}^{37}\text{ClCO}$ species we first estimated the upper state constants by adding to its ground state constants the differences between the upper states and ground state constants determined for the symmetrical species $^{35}\text{Cl}_2\text{CO}$. In this way a preliminary prediction was made allowing one to assign a few lines in the P- and R-branches with $K_a = 1, 2, 3$. Using these data more accurate upper state constants were determined allowing new assignments. Finally, as for the symmetrical species, the assignment process was iterated until no new assignment could be done. The band centers, rotational and centrifugal constants for the ground state and the 6^1 vibrational state of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ are given in Table 2. All the fits are very satisfactory since their standard deviations are of the order of the experimental

uncertainty (Table 3). Figures 2 and 3 show comparisons of the observed and calculated spectra. The good agreement between observation and simulation demonstrates the quality of the analysis and the fitting.

4. Summary.

Using a high-resolution Fourier transform spectrum an extensive analysis of the 22.5 μm spectral region of phosgene (Cl_2CO) has been performed. The upper state ro-vibrational energy levels of the 6^1 vibrational states of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ have been fit to within the experimental accuracy ($\sim 0.30 \times 10^{-3} \text{ cm}^{-1}$) using Watson-type Hamiltonians. In this way, accurate band centers, rotational and centrifugal distortion constants have been determined. As far as the intensities are concerned, more work is required to obtain more reliable band intensities from the very dense observed spectrum.

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Captions to figures:

Fig .1. Overview of the phosgene spectrum in the 22.5 μm spectral region.

The distinctive shape of the two A-type bands ν_6 of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$ with their narrow Q-branches are clearly recognizable. Upper trace: observed spectrum recorded with a resolution of 0.00102 cm^{-1} , an optical path length of 93.14 m, a phosgene pressure of $1.06 \pm 0.2\text{ hPa}$ and a stabilized temperature of 197 K. Lower traces: synthetic spectra, calculated at the same experimental conditions using the line lists generated in this work. The observed and synthetic spectra are in absorbance ($-\ln(I/I_0)$) and shifted vertically for clarity.

Fig. 2. Portion of the P-branch of the ν_6 bands of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$.

Upper trace: observed spectrum with the same experimental conditions as in Fig.1. Lower trace: synthetic spectrum calculated as in Fig.1. The series of $^{35}\text{Cl}_2\text{CO}$ P lines J d J, J-1 d+1 J-1,...with the d values are indicated on the figure. Note the splitting of lines for d = 5,6.

Fig. 3. Portion of the R-branch of the ν_6 bands of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$. Upper trace: observed spectrum with the same experimental conditions as in Fig.1. Lower trace: synthetic spectrum calculated as in Fig.1

Figure

Figure

Figure

Table 1. Watson-type Hamiltonian used to calculate the 6^1 states of phosgene $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$.

Table 2. Vibrational band centers, rotational and centrifugal distortion constant (in cm^{-1}) for the ground states and 6^1 vibrational states of phosgene $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$.

Footnotes:

^aUncertainties are given in parentheses in units of the last significant digits as stated, in terms of one standard deviation σ in the least squares adjustment.

^bFixed at ground state values.

Table 3. Range of quantum numbers observed for experimental energy levels of the vibrational states 6^1 of $^{35}\text{Cl}_2\text{CO}$ and $^{35}\text{Cl}^{37}\text{ClCO}$.

Table 1.

Watson-type Hamiltonian:

$$\begin{aligned}
H_W = E_v &+ \left[A^v - \frac{1}{2}(B^v + C^v) \right] J_z^2 + \frac{1}{2}(B^v + C^v) J^2 + \frac{1}{2}(B^v - C^v) J_{xy}^2 \\
&- \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 \mathbf{J}^2 - \Delta_J^v (\mathbf{J}^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 \mathbf{J}^2 \\
&+ H_K^v J_z^6 + H_{KJ}^v J_z^4 \mathbf{J}^2 + H_{JK}^v J_z^2 (\mathbf{J}^2)^2 + H_J^v (\mathbf{J}^2)^3 \\
&+ h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} \mathbf{J}^2 + 2h_J^v J_{xy}^2 (\mathbf{J}^2)^2 + \dots
\end{aligned}$$

with $\{A, B\} = AB + BA$, $J_{\pm} = J_x \mp iJ_y$ and $J_{xy}^2 = J_x^2 - J_y^2$.

Table 2.

	³⁵ Cl ₂ CO		³⁵ Cl ³⁷ Cl CO	
	0⁰ [6]	6¹	0⁰ [6]	6¹
E _v /hc		443.172062(15)		440.534956(17)
A x 10 ¹	2.641426020	2.636999872(350)	2.624420550	2.61993843(150)
B x 10 ¹	1.159121950	1.160273684(190)	1.127433880	1.128545467(880)
C x 10 ¹	0.8046257960	0.804951820(160)	0.7876964550	0.787967310(350)
Δ _K x 10 ⁶	0.3486464	0.3473470(1200)	0.344198872	0.3361706054(1600)
Δ _{JK} x 10 ⁷	-0.524752	-0.5265149(6500)	-0.50074582	-0.5122090(8200)
Δ _J x 10 ⁷	0.327238	0.33124722(7900)	0.309551360	0.3145185(1700)
δ _K x 10 ⁷	0.63436	0.6293590(6700)	0.60702511	0.614102(1000)
δ _J x 10 ⁷	0.1147183	0.11511353(3400)	0.108222604	0.10966010(9800)
H _K x 10 ⁸	0.0	b	0.0	b
H _{KJ} x 10 ¹¹	0.2961	b	0.2561449	b
H _{JK} x 10 ¹¹	-0.10618	b	-0.0837596	b
H _J x 10 ¹³	0.8556	b	0.8556	b
h _K x 10 ¹¹	-0.6995	b	-0.5166291	b
h _{KJ} x 10 ¹²	0.8414	b	0.8414 ^c	b

Table 3.

	³⁵ Cl ₂ CO	³⁵ Cl ³⁷ Cl CO
Vibrational State	6 ¹	6 ¹
J _{max}	77	71
K _{max}	34	33
Std, Deviation (10 ⁻³ cm ⁻¹)	0.30	0.43