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Integrated band intensities and absorption cross sections of phosgene (Cl₂CO) in the mid-infrared at 199, 250 and 300 K

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Abstract

Integrated band intensities and absorption cross-sections of phosgene (Cl_2CO) have been measured at different temperatures (199, 250 and 300 K) to support remote sensing applications, particularly for an accurate quantification of Cl_2CO in the Earth's atmosphere. To our knowledge and prior to this study, no previous work has examined the temperature dependence of the phosgene integrated band intensities. Series of N_2 -broadened spectra of phosgene were recorded from 525 to 2400 cm^{-1} , at a resolution of 0.1 cm^{-1} , using a Bruker IFS125HR Fourier transform spectrometer located at the LISA facility in Créteil, France. The pressure of each phosgene vapor sample was measured using high precision capacitance manometers and a minimum of six sample pressures were recorded for each temperature. The samples were introduced into an especially designed, short optical path length (5.10 ± 0.01 cm), coolable cell, that was mounted inside the spectrometer. From these spectra, integrated band intensities for six spectral regions corresponding to the ν_2/ν_4 , ν_5 , $\nu_2+\nu_6$, $\nu_2+\nu_5$, $2\nu_5$ and ν_1 bands were obtained from room temperature down to 199 K. We discussed and quantified error sources and, on average, the estimate accuracy for the measured integrated band intensities is equal to 4%. Measurements at room temperature were compared with previously reported values. Our results at 300 K, show an excellent agreement (better than 4%) with the Hopper *et al.* J Chem Phys (1968) values, agree reasonably well with those from the PNNL database (better than 9% for the stronger ν_1 and ν_5 bands of atmospheric interest), but depart strongly from the measurements of Lovell and Jones J Mol Spectrosc (1960) for which there are differences between 20 and 43%. In addition, our results at low temperatures show a non-negligible temperature dependence (7.5 to ~31%, depending on the bands, between 300 and 199 K), probably due to the presence of hot bands and possible overlapping neighboring bands such as overtones and combination/difference bands. To better understand these **temperature** variations a detailed high resolution investigation of pure Cl_2CO spectra over a wide range of temperature would be necessary.

Keywords: Phosgene; Cl_2CO ; Fourier transform infrared (FTIR) spectroscopy; Integrated band intensities; absorption cross sections; Temperature dependence; Earth's atmosphere

1. Introduction

Phosgene (Cl_2CO) is used as an industrial chemical in the manufacture of plastics, insecticides, pharmaceuticals, and herbicides. Its high toxicity and adverse effects required reducing its use over the years by working with safer substitutes [1]. In the Earth's atmosphere, phosgene is formed in the troposphere by OH-initiated oxidation of chlorinated hydrocarbons, namely : chloroform (CHCl_3), methylchloroform (CH_3CCl_3), trichloroethylene (C_2Cl_4) and tetrachloroethylene (C_2HCl_3) [1-4]. It is also formed in the stratosphere by the photochemical decay of carbon tetrachloride (CCl_4), as well as by oxidation of its tropospheric parent compounds [5,6]. With a lifetime of about 70 days, tropospheric phosgene is mostly removed by reaction in water droplets or by ocean deposition, whereas stratospheric phosgene, due to its weak absorption in the UV, is slowly oxidized to form ClO_x and has a lifetime of several years [1,3]. It is then one of the chlorinated compounds involved in stratospheric ozone depletion. It has been observed by stratospheric balloons using the solar occultation technique [6-8] and by satellite instruments such as the Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS) and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) for Cl_2CO vertical distribution retrievals [4,9,10]. For infrared remote sensing, the $11.8 \mu\text{m}$ ($830\text{-}860 \text{ cm}^{-1}$) spectral region is mainly used, but its strong absorption, corresponding to the ν_5 band, is masked by the ν_4 band of the Freon-11 (CFC-11 or CCl_3F), a greenhouse gas that absorbs strongly in the same spectral region. This interference leads to an overestimation of the concentration of CFC-11 in the atmosphere, if the absorption of Cl_2CO is not taken into account [8]. So, modelling the Cl_2CO contribution in atmospheric spectra is also essential to correct errors in CFC-11 retrievals.

Spectroscopically, phosgene is an asymmetric top molecule which, as listed in **Table 1**, has six infrared fundamental vibrational modes: two in the mid-infrared ν_5 (851.013 cm^{-1}) and ν_1 (1828.202 cm^{-1}) and four low energy modes at 301.546 cm^{-1} (ν_3), 443.172 cm^{-1} (ν_6), 572.526 cm^{-1} (ν_2) and 582.089 cm^{-1} (ν_4). Its rotational constants have been determined for the ground and first excited states by various microwaves studies [15-21]. Among the fundamental vibrational modes, ν_1 and ν_5 bands are of major interest since they are used for the remote sensing of Cl_2CO , thanks to their strong absorption in the atmospheric “windows” located at 5.5 and $11.8 \mu\text{m}$, respectively. However, in addition to the infrared active fundamentals, the spectrum of Cl_2CO contains various overtones, combinations and hot bands that originate from the states below 600 cm^{-1} (ν_2 , ν_3 , ν_4 and ν_6). Due to these low energy states, the Cl_2CO

cold bands are expected to be overlapped by many hot bands which contribute significantly to the absorption. Indeed, only ~58% of the population is in the ground state at 300 K (see **Table 1**). As a consequence the infrared spectrum of Cl₂CO is very crowded at room temperature. At 199 K, the ground state population is 82% and thus hot bands are strongly reduced, compared to the situation at room temperature. This is an important point when estimating the contribution of hot bands to the band intensity. This is why in order to reduce the spectral density and then facilitate the spectroscopic analysis, high-resolution studies of the fundamentals of phosgene, considering both the ³⁵Cl₂CO and ³⁵Cl³⁷ClCO isotopologues, have been carried out at low temperatures [**11-14, 22**]. From these studies, very accurate band centers, rotational, centrifugal distortion and interaction constants have been determined for the six vibrational states of the two isotopologues of Cl₂CO.

Besides these spectroscopic studies dealing with line positions, the quantitative intensity aspect needs to be investigated for this molecule. However measuring individual Cl₂CO transitions line-by-line is extremely challenging, even at low sample pressures and with Doppler-limited resolution because, as already said the phosgene spectrum is very dense: Three isotopologues, strong hot bands, etc. A more realistic approach for quantitative measurements is then to determine integrated band intensities and/or cross-sections which are of interest for atmospheric remote sounding applications. Up to now and to the best of our knowledge, three studies have published integrated band intensities of Cl₂CO at room temperature [**23-25**]. However, according to Toon *et al.* [**8**], further laboratory measurements of the integrated band intensities of the mid-infrared bands of Cl₂CO as a function of temperature are needed, on the one hand to resolve the large discrepancies between the existing room temperature measurements [**23-25**], and on the other hand to understand the contribution of hot bands. Indeed, according to Toon *et al.* [**8**], not taking into account properly the hot bands contributions leads to a systematic error of ~20% on the concentrations of phosgene retrieved from atmospheric spectra. In order to help solving the questions raised previously the present work reports at temperatures of 199, 250 and 300 K accurate integrated band intensities derived from laboratory spectra covering the spectral range 525-2400 cm⁻¹. In the next chapters we describe the measurements, estimate their accuracy, and compare the results with the previous sets of measurements at room temperature [**23-25**].

2. Experimental details

Absorption spectra of phosgene have been recorded in the range 525 to 2400 cm^{-1} using the high-resolution Bruker IFS125HR Fourier transform spectrometer (FTS) located at the LISA facility in Créteil (France). The instrument was equipped with a silicon carbide Globar source, a KBr/Ge beamsplitter and a liquid nitrogen cooled HgCdTe (MCT) detector. The diameter of the entrance aperture of the spectrometer was set to 3.15 mm to maximize the intensity of infrared radiation falling onto the MCT detector without saturation or loss of spectral resolution. Interferograms were recorded with a 40 kHz scanner frequency and a maximum optical path difference (MOPD) of 9 cm. According to the Bruker definition (resolution = $0.9/\text{MOPD}$), this corresponds to a resolution of 0.1 cm^{-1} . The spectra were obtained by Fourier transformation of the averaged interferograms (100 scans) using a Mertz phase correction with a 1 cm^{-1} resolution, a zero-filling factor of 2 and no apodization (boxcar option).

For the measurements, a small cryogenic cell ($5.10 \pm 0.01 \text{ cm}$ path length) was used, a schematic viewcut of which is given in **Figure 1**. The cell is made of stainless steel, to minimize adsorption and corrosion issues, and fitted with 9.5 mm diameter, 0.4 mm thick, wedged diamond windows (E6, Netherlands). The cell is surrounded by an outer stainless steel jacket, in which cold nitrogen (N_2) gas is flowed in and out (**Figure 1**). The temperature control is obtained mainly by varying the cold gas flow rate, but a minor correction can be obtained using an additional heating element (Thermocoax, France) wrapped around the gas cell itself. The temperature measurement is made with four separate Pt-100 sensors: one is inserted in the gas to be measured, a few millimeters above the infrared beam, two others are placed on different sides of the cell body, and a fourth one on the gas tube inlet used for filling the cell. The whole assembly is placed directly inside the sample compartment of the spectrometer, and the vacuum level inside the spectrometer is thus critical to avoid spurious ice absorptions. The FTS was thus evacuated below $3 \times 10^{-4} \text{ hPa}$ by an all-magnetic bearing turbomolecular pump in order to minimize absorption by atmospheric gases while avoiding excessive mechanical vibrations.

Triphosgene was purchased from Sigma Aldrich and heated to generate phosgene. Phosgene production begins at a temperature of 80°C , below which the gas is not produced. The reaction proceeds cleanly up to 110°C at a steady rate. Before use, the sample was purified at -130°C by freeze-and-thaw cycles to remove any non-condensable impurities. Samples were prepared afterwards by applying the following procedures: first, a mixture of 1.7% Cl_2CO in nitrogen (Air Liquide, France, 99.9998% purity) was prepared; next, the

sample was stabilized for two hours to obtain a dilute and homogeneous sample; and from this, an amount, corresponding to the desired Cl₂CO amount, was extracted and diluted with about 500 hPa of nitrogen as a broadening gas. Six samples were introduced in the cell at 199 ± 1 K, nine samples at 250 ± 1 K, and six samples at 300 ± 1 K. The sample pressure in the cell was measured using a precision capacitive pressure gauge (MKS Baratron, USA, 10 and 1100 hPa ranges) with a reading accuracy of 0.12% according to the manufacturer's specification. Considering the uncertainty arising from small variations of the pressure during the recording (~ 0.8%), we estimated the measurement uncertainty on the pressure to be equal to 1%. A summary of the experimental conditions is provided in **Table 2**. Each spectrum was ratioed against a background spectrum of the empty cell, which was recorded at a resolution of 0.1 cm⁻¹ with a large number of scans, in order to ensure the best possible signal-to-noise in the ratioed spectra.

Figure 2 gives an overview of the N₂-broadened Cl₂CO spectrum recorded at 300 K (spectrum S1 in **Table 2**). As displayed in **Figure 2**, the observed bands are ν_2/ν_4 at 577.31 cm⁻¹, ν_5 at 851.01 cm⁻¹, $\nu_2+\nu_6$ at 1014.78 cm⁻¹, $\nu_2+\nu_5$ at 1414.92 cm⁻¹, $2\nu_5$ at 1681.38 cm⁻¹, and ν_1 at 1828.20 cm⁻¹. Note a small impurity of CO₂ observed in the spectrum with the spectral feature at 2350 cm⁻¹ corresponding to the ν_3 band of CO₂. As the total sample pressure P_t includes CO₂ impurity, it is thus required to assess the CO₂ partial pressure contribution in order to determine the true Cl₂CO partial pressure. To calculate the CO₂ partial pressure, the ν_3 band intensity 9.07×10^{-17} cm⁻¹/molecule.cm⁻² reported in Ref. [26] was used. The calculated CO₂ partial pressure P_{CO_2} was then used to determine the partial pressure $P_{\text{Cl}_2\text{CO}}$ of phosgene in the sample. Pressure values for all the samples are reported in **Table 2**.

3. Integrated band intensities and uncertainty assessment

3.1 Determination of the integrated band intensities

Absorption measurements were performed for various pressures to determine the integrated intensities for all bands of phosgene indicated above i.e. ν_2/ν_4 , ν_5 , $\nu_2+\nu_6$, $\nu_2+\nu_5$, $2\nu_5$ and ν_1 . The derived integrated absorbances A_{int} (cm⁻¹) are plotted as a function of the Cl₂CO partial pressure and show a clear linear dependence to pressure (**Figure 3**). For all selected spectral regions, high correlation coefficients of ~0.99 are obtained. The slope of the linear fit A (cm⁻¹/hPa) is used to determine the integrated band intensity A (cm⁻¹/molecule.cm⁻²), according to the following equation:

$$A (\text{cm}^{-1}/\text{molecule} \cdot \text{cm}^{-2}) = \frac{2.3 \times A (\text{cm}^{-1}/\text{hPa}) \times P_{\text{atm}} \times T}{N \times l \times T_0} \quad (1)$$

Where $N = 2.68676 \times 10^{19}/\text{cm}^3$ is the Loschmidt number at standard conditions, $P_{\text{atm}} = 1013.25 \text{ hPa}$, $T_0 = 273.15 \text{ K}$, $l = 5.10 \text{ cm}$, T is the measurement temperature in K and $A (\text{cm}^{-1}/\text{hPa})$ the spectral integrated intensity measured in decadic absorbance and normalized to the partial pressure.

Wavenumber integration limits, retrieved values of the integrated band intensities for the three measurement temperatures, 199, 250 and 300 K and corresponding uncertainties are listed in **Table 3**. Also for comparison, values derived at 300 K, from the PNNL database [25], Hopper *et al.* [23] and Lovell and Jones [24] are given (See section 4 for a detailed discussion).

3.2 Uncertainty assessment

Examination of the standard deviations of the fits shows that they are generally less than 3.5% (see **Figure 4**) for all temperatures. However, estimating the accuracy of the measured integrated band intensities requires considering the uncertainties effecting all physical parameters and contributions from possible systematic errors [25, 27] together with the standard deviation of the fits. These various sources of error and their associated uncertainties, expressed relative to the integrated band intensities, are given in **Figure 4**, for all the bands studied in this work at 300K. It is clear that the systematic errors and the standard deviations of the fits are the main sources of errors. These contributions are also predominant for the remaining two low temperatures which are not illustrated here. The dominant contributions to systematic errors come from the location of the 100 and 0% transmission photometric levels, as well as from the electronic and detector nonlinearities [25, 27]. A realistic assessment of systematic photometric errors is not an easy task and probably strongly depends on the setup used. We base our present estimate on the arguments developed in Ref. [25] using instruments comparable to ours. In particular, HgCdTe detectors are used for their high sensitivity, but are also known for their deviation to a linear behavior. When using an HgCdTe for mid-infrared measurements, deviations up to 2.3% on retrieved band intensities were found when compared to that derived using more linear detectors such as InSb or DTGS ones. We therefore retained a 3% value for the contribution of systematic errors. For each band, we have then estimated the accuracy of the integrated band intensities from the uncertainties on the individual experimental parameters, i.e. ε_{si} (sample purity), ε_t

(temperature), ε_p (pressure), ε_{pl} (path length), ε_{fit} (standard deviation from fit) and ε_{sys} (systematic errors), assuming that these uncertainties are uncorrelated:

$$\varepsilon = \sqrt{\varepsilon_{si}^2 + \varepsilon_t^2 + \varepsilon_p^2 + \varepsilon_{pl}^2 + \varepsilon_{fit}^2 + \varepsilon_{sys}^2} \quad (2)$$

Using this equation and the experimental relative uncertainties involved, the estimated overall uncertainty (estimated accuracy) for each of the integrated band intensity measured was calculated. They vary from 3.4 to 6.2% but, on average, the estimated accuracy on the reported integrated band intensity is equal to 4%, and this for the three temperatures considered in this work.

3.3 Variations of the absorption spectra and of integrated band intensities with respect to temperature

Examples of the absorption cross sections measured in this work, for all observed bands are presented in **Figures 5** and **6** for $T = 199$ and 300 K. As can be seen, when decreasing the temperature, the absorption peaks increase and sharpen leading to a reduction of the absorption widths of the bands. One can see this effect very well in the spectral region of the ν_5 band. It is mainly due to the variations in the vibrational and rotational populations with temperature. It is also worth noticing that hot bands persist in the spectra even for the coldest temperature since their contributions are still amounting to 18% at 199 K (see **Table 1**).

Figure 7 presents the temperature dependence of the measured integrated band intensities for the various phosgene bands. Changing the temperature from 300 to 199 K leads to non-negligible variations in the integrated band intensities with maximum differences reaching 31% for the weak $\nu_2+\nu_5$ band. Even if these variations are higher than our expected measurement uncertainties, it is difficult to assess if the integrated band intensities are temperature-dependent or not. Indeed, for the ν_1 , ν_2/ν_4 and ν_5 bands, the variations are less than 10%. **Such variations have been observed in the literature for similar heavy molecules. For example, for the N_2O_5 molecule, deviations of 6 to 10% are observed in the values of the integrated band intensities when the temperature varies from 233 to 296 K [28]. For $ClONO_2$, deviations of 6 to 31% are observed in the values of the integrated band intensities when the temperature varies from 213 to 296 K [29]. The largest difference (31%) was observed for a very weak band, as in our study. Finally, for the $BrONO_2$ molecule, a deviation of 27% was observed in the value of the relative absorption cross sections when the temperature varies**

from 213.9 to 293.3 K [30]. More generally, the precise determination of integrated band intensities for reactive or adsorbing volatile organic compounds at variable temperatures poses specific experimental challenges and our results calls for a few remarks. Two procedures can be used: if only the pure absorber gas is introduced in the cell, given the needed pressure range, thermomolecular effects can distort the pressure reading, especially for relatively low pressures (a few hPa). Instead, if, as we chose to do in this study, the absorbing gas is introduced from a previously done mixture with an inert buffer gas, the error on the total gas pressure will be relatively small, as the total pressure is high (hundreds of hPa range), however the partial pressure of the absorbing gas can no longer be directly measured. This may be a problem if the molecule can adsorb on the cell walls, an effect which depends on the cell wall nature and probably, to some extent, on the temperature. This probably affects our measurements, especially the first two data points at low partial pressures (1.894 and 2.439 hPa) but, above these pressures, data points present a consistent linear dependence. We have retained all data to illustrate this difficulty, but use only the higher pressure data points for the determination of band region integrated intensities. The second comment relates to the apparent temperature dependence of the band region integrated intensities. It is expected that the fundamental band region integrated intensities should not present such dependences, as it is expected that fundamental bands (ν_i) and their associated hot bands ($2\nu_i - \nu_i$ and so on) should have the same transition moment (neglecting anharmonicity). In practice, it seems not always to be the case, as other transitions can fall by chance in the vicinity of the fundamental transitions and have different temperature dependences than that of the fundamentals. These can be difference bands of the type $(\nu_i + \nu_j) - \nu_k$. For instance, if the weak features observed on the high frequency side of the ν_1 band is obviously not a cold band (perhaps $\nu_5 + \nu_2 - \nu_6$), other small features show a marked, although different temperature dependences. The feature near 977 cm^{-1} is likely to be the $\nu_1 - \nu_5$ difference band and its linear decrease with temperature is consistent with the calculated decrease in $\nu_5 = 1$ state population. The weak feature near 827 cm^{-1} is likely to be the $\nu_1 - (\nu_2 + \nu_6)$ as it clearly presents a higher order temperature dependence. This is consistent with the expected decrease in $\nu_2 = \nu_6 = 1$ vibrational state population and the experimentally observed temperature decrease for this spectral region (see **Figure 5**, middle trace). This was discussed, for instance, for measurements of acetone at variable temperatures [31]. A later study alleviated this problem by simply renormalizing all integrated band intensities on those deduced from PNNL spectra measured at room temperature [32]. We chose to avoid this procedure to propose a new, independent measurement. It is however clear that a better, more precise intensity determination should

proceed through a line-by-line analysis from high resolution spectra at variable temperature, cold enough to eliminate hot bands and preferably with monoisotopic molecules. This goes, however, much beyond the scope of our present study. To summarize, the integrated band intensity of each band system should in principle be independent of temperature. However, overlapping weak features arising from neighboring bands such as combination/difference and hot bands can be responsible for small variations of the integrated intensities with temperature. In fact, each spectral region presents a specific temperature dependence, which cannot be clearly understood in absence of a complete spectral assignment of all unresolved weaker features. To investigate this dependence, it would be necessary to record pure Cl₂CO high resolution spectra at low and room temperatures.

4. Comparison with previous works at room temperature

Table 3 reports the phosgene integrated band region intensities derived in this work for the three measurement temperatures, 199, 250 and 300 K and values derived at 300 K from the PNNL database [25], Hopper *et al.* [23] and Lovell and Jones [24]. Our results agree reasonably well (better than 9%) with the PNNL data [25], and are consistent within the combined measurement uncertainties (**Figure 8**), except for the weak bands ν_2/ν_4 , $\nu_2+\nu_5$ and $\nu_2+\nu_6$ where the PNNL results are higher by 14.1%, 16.4% and 14.5%, respectively. On the other hand, an excellent agreement (better than 4%) is observed with the values from Hopper *et al.* [23]. Finally a strong disagreement is observed when comparing with the values from Lovell and Jones [24] which exhibit 20 to 43% discrepancies with our results and also with those of Hopper *et al.* [23] and the PNNL data [25]. As a conclusion one can say that three measurements are consistent and therefore that the results of Lovell and Jones [24] can likely be discarded.

5. Summary

Integrated band intensities of phosgene have been measured in the 525-2400 cm⁻¹ spectral region at 199, 250 and 300 K. The measurements were performed by recording N₂-broadened spectra at a resolution of 0.1 cm⁻¹, over a wide range of pressures, using Fourier transform infrared spectroscopy. Our results at room temperature were compared with previously published measurements. The results from this work show an excellent agreement (better than 4%) with the results of Hopper *et al.* [23] and are consistent to within their combined

measurement uncertainties with the PNNL data [25]. On the contrary they disagree with the measurements of Lovell and Jones [24] with a maximum difference of ~43%. With respect to the temperature, the integrated band intensities show a non-negligible dependence (7.5 to ~31%), when decreasing temperature from 300 to 199 K, probably due to the presence of overlapping weak features arising from neighboring bands such as overtones, combination/difference and hot bands. It would be important to check this assumption by recording high resolution pure samples of Cl₂CO over the range of temperatures used for the present measurements.

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