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## The $\nu_1$ , $\nu_2$ , and $\nu_3$ bands of carbonyl chlorofluoride (COFCl) at 5.3, 9.1, and 13.1 $\mu\text{m}$ : position and intensity parameters and their use for atmospheric studies

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### ABSTRACT

A list of line positions and, for the first time, of line intensities was generated for the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  fundamental bands of the  $^{12}\text{C}^{16}\text{O}^{35}\text{Cl}$  and  $^{12}\text{C}^{16}\text{O}^{37}\text{Cl}$  isotopologs of carbonyl chlorofluoride, located at 5.3, 9.1, and 13.1  $\mu\text{m}$ , respectively. In addition, for the most abundant isotopolog ( $^{12}\text{C}^{16}\text{O}^{35}\text{Cl}$ ) this list includes also the contributions from the first two associated hot bands. The parameters included in this database were generated by combining the results of previous experimental analyses and ab initio calculations [Perrin A, Flaud JM, Bürger H, Pawelke G, Sander S, Willner H. First high resolution analysis of the six fundamental bands  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  of  $\text{COF}^{35}\text{Cl}$  in the 340 to 2000  $\text{cm}^{-1}$  region. *J Mol Spectrosc* 2001;209:122–232; Demaison J, Perrin A, Bürger H. Ab initio anharmonic force field and equilibrium structure of carbonyl chlorofluoride. *J Mol Spectrosc* 2003;221:47–56]. For the purpose of the present work, a partial re-investigation of the  $\nu_1$  of  $\text{COF}^{35}\text{Cl}$  was performed, together with the first identification of the  $\nu_2$  band of  $\text{COF}^{37}\text{Cl}$ .

These parameters were generated in order to improve the quality of remote sensing of the atmosphere in the mid-IR. Analyses of atmospheric solar occultation spectra measured by the JPL MkIV interferometer show that the new list not only improves the quality of retrievals of COFCl, but also of several other gases whose absorptions overlap those of COFCl.

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## 1. Introduction

### 1.1. Atmospheric interest

Because of the implication of the chlorofluorocarbons (CFCs) in atmospheric ozone depletion in the earth's atmosphere, a number of measurements were performed to determine the concentration of halogen containing compounds in the stratosphere. Of the various possible oxidation products of CFCs in the stratosphere, carbonyl

chlorofluoride (COFCl) receives some attention since it is an important reservoir of chlorine and fluorine in the Earth's atmosphere [1–8]. It is probable that the major source of atmospheric COFCl is CFC-11 (trichlorofluoromethane,  $\text{CCl}_3\text{F}$ ). Although CFC-12 (difluorodichloromethane,  $\text{CCl}_2\text{F}_2$ ) is the most abundant fluorine-containing source gas, it most likely breaks down to form carbonyl difluoride ( $\text{COF}_2$ ) instead of COFCl. This is because CFC's oxidation in the stratosphere occurs by breaking of the C–Cl bonds before any C–F bond is cleaved [7,8], while in the case of HCFCs, the C–H bond breaks first.

Satellite-based remote sensing measurements performed by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) for a time period

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spanning February 2004 through April 2007, have been used to achieve retrievals of COFCl [6–8]. Later on, a reanalysis of these ACE-FTS measurements was performed and compared with those from the ATMOS experiment during the Spacebab-3 (1985) and ATLAS-1 (1992) Space Shuttle missions to study the global distribution of COFCl [8]. These measured profiles were compared with predictions from the Atmospheric and Environment Research (AER), Inc 2D model which was modified to account for COFCl [9–11]. A major source for atmospheric COFCl appears in the stratosphere over the tropics, likely related to the higher levels of the parent molecule (CCl<sub>3</sub>F) and insolation in this region.

### 1.2. The ATMOS linelist for COFCl

The main goal of the present study is to provide a new and more accurate COFCl linelist. It is now time to evaluate the COFCl line parameters from the ATMOS supplemental linelist [12,13] which have been used for all COFCl atmospheric retrievals to date. Indeed, up to now, COFCl is missing in the HITRAN [14] or GEISA [15] linelists.

The very crude COFCl linelist in the ATMOS database [12,13] was generated at 5.3 and 13.1 μm using laboratory spectra of natural COFCl recorded at 0.020 cm<sup>-1</sup> resolution and at room temperature [16]. No information on the isotopic structure (COF<sup>37</sup>Cl versus COF<sup>35</sup>Cl) could be obtained at this resolution, and the ATMOS list is, by default, restricted to the “main” isotopolog, COF<sup>35</sup>Cl. All COFCl intensities are set with an uncertainty factor of three in the absence of line intensity measurements or calculation. This linelist was made solely for the purpose of trying to detect atmospheric COFCl. It was intended that in the event of a positive detection, a better COFCl linelist would be generated. The 5.3 and 13.1 μm regions correspond to the strong ν<sub>1</sub> band and to the four times weaker ν<sub>3</sub> band, respectively, centered at 1875.8 and 764.4 cm<sup>-1</sup>, respectively, for COF<sup>35</sup>Cl [17]. At 13.1 μm, the linelist involves only 413 lines in the 764.11–764.72 cm<sup>-1</sup> spectral region. At 5.3 μm, no rotational assignment is given for the ν<sub>1</sub> band, and each of the 2036 lines is reported with a single lower state energy ( $E''=345\text{ cm}^{-1}$ ). Finally, this list does not include parameters for the ν<sub>2</sub> band of COFCl located at 1095.0646 cm<sup>-1</sup> for COF<sup>35</sup>Cl [17], which is the strongest IR band, almost ~30% stronger than the ν<sub>1</sub> band.

To our knowledge, no line broadening or shifting parameters data exist in the literature for COFCl. Therefore, typical values of the air broadening coefficient of 0.1 cm<sup>-1</sup> atm<sup>-1</sup> and temperature dependence  $\gamma(T)=\gamma(T_0)(T/T_0)^{-0.75}$  are quoted in the ATMOS list. In the continued absence of data for line shape description, the same choice will be adopted here.

The rather poor quality of these parameters is linked to the experimental difficulties in recording laboratory spectra for COFCl. Indeed, as it is underlined in Refs. [17,18]

this dangerously poisonous molecule is difficult to produce and handle safely under laboratory conditions.

Also, in order to enable a possible analysis, laboratory spectra must be recorded at higher resolution, and if possible, for a pure isotopic sample (COF<sup>35</sup>Cl) of carbonyl chlorofluoride. This is because the infrared spectrum is very crowded owing to the small values of the rotational constants ( $A\sim 0.395$ ,  $B\sim 0.176$  and  $C\sim 0.122\text{ cm}^{-1}$  for COF<sup>35</sup>Cl) and because of the significant contribution of the hot bands to the observed absorption, even at room temperature. This last point will be discussed later in the text.

### 1.3. Existing high resolution microwave or infrared studies of COFCl

Carbonyl chlorofluoride (COFCl) is a planar C<sub>s</sub> type molecule. Its microwave spectrum was investigated in great detail, leading to a good knowledge of the rotational energy levels of this molecule in the ground vibrational state for several isotopologs [19–21]. The COFCl equilibrium structure and the quadratic, cubic and semi-diagonal quartic force field of O=CFCI have been derived in Ref. [18]. For this purpose, experimental ground state rotational constants were combined with rovibrational interaction parameters obtained from ab initio calculations performed at the MP2 level of theory and employing a basis set of triple-zeta quality. This molecule has six vibrational modes which are quoted in Table 1 together with their vibrational energies for both <sup>12</sup>C<sup>16</sup>O<sup>35</sup>Cl and <sup>12</sup>C<sup>16</sup>O<sup>37</sup>Cl. Table 1 gives also the type of the infrared fundamental bands. For symmetry reasons, only C-type transitions are allowed for the ν<sub>6</sub> band. On the other hand, infrared bands like ν<sub>1</sub>, ν<sub>2</sub>, ν<sub>3</sub>, ν<sub>4</sub> and ν<sub>5</sub>, are in principle hybrid, with both A-type ( $\Delta|K_a|=even$ ,  $\Delta|K_c|=odd$ ) and B-type ( $\Delta|K_a|=odd$ ,  $\Delta|K_c|=odd$ ) transitions. In fact, ν<sub>3</sub> is an A-type band, while both ν<sub>4</sub> and ν<sub>5</sub> are B-type bands [17,18]. On the other hand, ν<sub>1</sub> and ν<sub>2</sub> are hybrid bands, and therefore particularly crowded.

The extensive analysis of the six fundamental bands of COF<sup>35</sup>Cl [17] and of the ν<sub>3</sub> and ν<sub>4</sub> bands of COF<sup>37</sup>Cl [18] was performed using high resolution ( $\leq 0.003\text{ cm}^{-1}$ ) Fourier transform spectra of COFCl recorded on the Bruker spectrometer of the University of Wuppertal. For this purpose, natural and COF<sup>35</sup>Cl isotopically enriched samples of carbonyl chlorofluoride were prepared using the methods described in Ref. [17]. This study was completed by the identification of several combination or overtones bands of COF<sup>35</sup>Cl, using additional Wuppertal FTS infrared spectra recorded at low resolution in the 1000–7000 cm<sup>-1</sup> spectral region [18]. Details on the experimental conditions used to record the spectra and on the ab initio calculations are given in Refs. [17,18].

Table 3 of Ref. [17] and Table 11 of Ref. [18] detail the results of these infrared analyses and of the energy levels calculations which were difficult. For this heavy molecule, the spectrum is very dense. This is particularly the case for the ν<sub>1</sub> and ν<sub>2</sub> bands which are hybrid, and therefore particularly crowded. In addition these two bands are significantly perturbed.

<sup>1</sup> In the following COF<sup>35</sup>Cl and COF<sup>37</sup>Cl refer to the <sup>12</sup>C<sup>16</sup>O<sup>35</sup>Cl and <sup>12</sup>C<sup>16</sup>O<sup>37</sup>Cl isotopologs, respectively.

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