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Structure and conformational analysis of CFC-113 by density functional theory calculations and FTIR spectroscopy

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Abstract

Altitude-resolved volume mixing ratio profiles of CFC-113 have recently become available on a global scale with the Atmospheric Chemistry Experiment (ACE) satellite mission. However, the accuracy of the retrieval is currently limited by the uncertainties on the spectroscopic parameters of CFC-113. This paper reports on the geometrical structure, harmonic frequencies and intensities in the mid-infrared region of the two conformers of CFC-113 and the evaluation of whether theoretical calculations reproduce measurements. The calculations are performed using density functional theory at the B3LYP/6-311+G(3df) level. The molecular geometry parameters, the enthalpy difference and the potential barrier between conformers are calculated. The harmonic frequency of the normal modes of vibration are presented and accurately compared to experimental data. Overtones and combination bands are assigned in the 1200–2500 cm^{-1} region.

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1. Introduction

CFC-113 (1,1,2-trichlorotrifluoroethane) is the third most abundant chlorofluorocarbon in the atmosphere. Its ozone depletion potential has led to its ban by the Montreal Protocol and its subsequent amendments. Although its emission is now controlled by international regulations, the long lifetime of this compound (~85 years) makes its monitoring essential, as the average concentration of CFC-113 in the atmosphere is still approximately 80 ppt. The impact of this molecule on the ozone layer and its contribution to enhanced global warming require precise measurement of its concentration worldwide for assessing theoretical predictions and for assessment of the effectiveness of international regulations. Recently, the Atmospheric Chemistry Experiment (ACE) satellite mission [1] has provided the first space-based atmospheric measurements of CFC-113 on a global scale [2]. However, the uncertainties in the spectroscopic parameters currently available for this molecule compromise the accuracy of the retrievals. The errors associated with spectroscopic data have been evaluated to be at least 20% [3].

Only a few attempts have been made to characterize the optical properties of CFC-113 in the vapour phase. The most recent [4], published in 1987, presented an extensive experimental study of CFC-113 in the solid, liquid and gaseous phases. An assignment of the C_1 and C_s conformers supported by a normal coordinate calculation involving related molecules was carried out. Although the comparison between theory and experiment was quite good, discrepancies existed in the 800–1250 cm^{-1} region. Because this region is of considerable interest in atmospheric science, it is crucial to verify

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the line attribution in the vapour phase and to perform a new theoretical calculation of CFC-113 parameters using modern tools.

The main purpose of this work is to provide theoretical infrared spectroscopic properties of the two conformers of CFC-113 and to determine whether those results are in good agreement with experimental data. The calculations are performed by density functional theory using the Gaussian 03 software [5]. Frequency assignments and analysis of intensities are presented.

2. Computational and experimental background

Time-dependent density functional theory has become the most widely used method for determination of the molecular parameters of medium-sized molecules. It outperforms the Hartree–Fock theory by including electron correlation correction and offers an accuracy comparable to second-order Møller–Plesset theory (MP2) at a considerably lower computational cost. We are thus able to use a large basis set, including the diffuse polarization functions. The 6-311+G(3df) basis set represents a good compromise between accuracy and computational cost (only one set of diffuse and polarization functions is required as CFC-113 does not contain any hydrogen bonds). We used the well-known Becke's three-parameter exchange functional coupled with the non-local correlation from the Lee, Yang, and Parr functional (B3LYP). This recognized hybrid functional is probably the most widely used and remains the standard reference in DFT calculation [6]. The geometry optimizations and harmonic vibrational frequencies calculation are carried out simultaneously with B3LYP/6-311+G(3df).

Our theoretical results have been compared to experimental data taken in our laboratory by absorption Fourier transform infrared (FTIR) spectroscopy. The spectrometer is a Bomem DA8.002 equipped with a KBr beamsplitter and operating with a Globar source. A 25-cm-long stainless steel gas cell, mounted with ZnSe windows, is positioned between the spectrometer and a MCT (mercury–cadmium–telluride) detector. To remove non-linear Beer–Lambert effects on strong bands, an extrapolation to 0-torr (the optically thin limit) is performed from acquisitions taken at pressures varying from 0.2 to 2 torr.

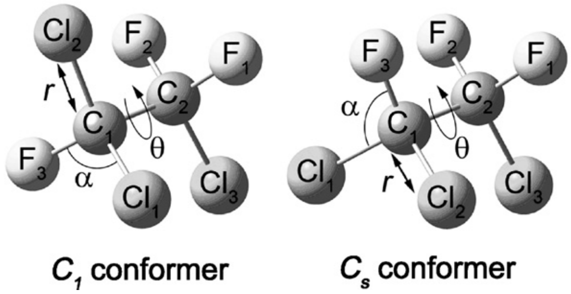

Fig. 1. The two geometrical conformations of CFC-113. r represents the interatomic distance (in Å); α, the angle between adjacent bonds; and θ, the dihedral angle (both in degree).

Table 1
Calculated structural parameters of the two CFC-113 conformers

	C_1 conformer	C_s conformer
$r(C_1,C_2)$	1.57	1.57
$r(C_1,F_3)$	1.34	1.35
$r(C_1,Cl_1)$	1.77	1.77
$r(C_1,Cl_2)$	1.78	1.77
$r(C_2,F_1)$	1.33	1.34
$r(C_2,F_2)$	1.34	1.34
$r(C_2,Cl_3)$	1.77	1.77
$\alpha(C_2,C_1,F_3)$	107.97	106.22
$\alpha(C_2,C_1,Cl_1)$	111.01	110.88
$\alpha(C_2,C_1,Cl_2)$	109.19	110.88
$\alpha(F_3,C_1,Cl_1)$	109.30	108.63
$\alpha(F_3,C_1,Cl_2)$	108.68	108.63
$\alpha(Cl_1,C_1,Cl_2)$	110.62	111.41
$\alpha(C_1,C_2,F_1)$	109.78	108.24
$\alpha(C_1,C_2,F_2)$	108.56	108.24
$\alpha(C_1,C_2,Cl_3)$	111.76	113.42
$\alpha(F_1,C_2,F_2)$	108.32	107.74
$\alpha(F_1,C_2,Cl_3)$	109.62	109.51
$\alpha(F_2,C_2,Cl_3)$	108.71	109.51
$\theta(F_3,C_1,C_2,F_1)$	180.00	58.22
$\theta(F_3,C_1,C_2,F_2)$	61.76	−58.30
$\theta(F_3,C_1,C_2,Cl_3)$	−58.14	179.96
$\theta(Cl_1,C_1,C_2,F_1)$	−60.21	176.06
$\theta(Cl_1,C_1,C_2,F_2)$	−178.45	59.54
$\theta(Cl_1,C_1,C_2,Cl_3)$	61.65	−62.20
$\theta(Cl_2,C_1,C_2,F_1)$	62.01	−59.63
$\theta(Cl_2,C_1,C_2,F_2)$	−56.23	−176.14
$\theta(Cl_2,C_1,C_2,Cl_3)$	−176.13	62.12

Interatomic distances (r) are in Å, angles (α) and dihedral angles (θ) in degrees. The position of atoms is given in Fig. 1.

3. Structure and enthalpy of the two CFC-113 conformers

CFC-113 has two geometrical conformations related to each other by a rotation of about 120° around the C–C single bond as illustrated in Fig. 1. One of the conformers, characterized by a *trans* position of two C–Cl and C–F bonds, has a C_1 symmetry while the other one, characterized by a *gauche* position of all the C–Cl and C–F bonds, has a C_s symmetry.

The results of our geometrical optimization for both conformers are presented in Table 1. The distances between the atoms are little affected by the conformational symmetry, with a C–C distance of 1.57 Å, and average C–Cl and C–F distances of 1.77 and 1.34 Å, respectively, for both configurations. We can note that the C_s conformation presents a more symmetrical structure, with identical angles and distances on the C–Cl bonds of the $CFCl_2$ group and C–F bonds of the CF_2Cl group.

We calculated an enthalpy difference between the two conformers of 133.6 cm^{-1}, with the C_1 structure being the more stable form. This value is in the range of those obtained by electron diffraction (94.5 ± 87.8 cm^{-1} [7])