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Microwave, structural, conformational, vibrational studies and ab initio calculations of fluoroacetyl chloride



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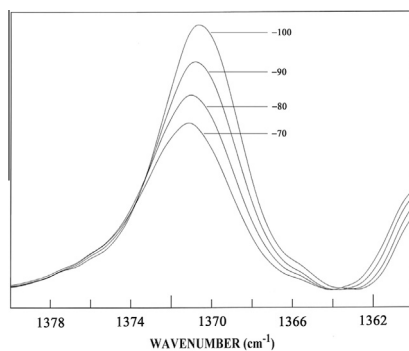
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HIGHLIGHTS

- The most stable trans conformer has been identified from microwave spectra.
- Enthalpy difference has been determined between the three forms.
- Adjusted r_0 structures were obtained for trans form.
- Ab initio calculations were performed for the three conformers.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared and Raman spectra ($3200\text{--}50\text{ cm}^{-1}$) of the gas, liquid or solution, and solid of fluoroacetyl chloride, FCH_2COCl have been recorded. FT-microwave studies have also been carried out and 22 transitions were recorded for the trans conformer. Variable temperature (-50 to $-105\text{ }^\circ\text{C}$) studies of the infrared and Raman spectra ($3200\text{--}50\text{ cm}^{-1}$) of xenon solutions have been carried out. From these data, the trans, cis and gauche conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined to be $159 \pm 11\text{ cm}^{-1}$ ($1.90 \pm 0.14\text{ kJ mol}^{-1}$) with the trans conformer the more stable form than the cis. The energy difference between the cis and gauche form is $222 \pm 18\text{ cm}^{-1}$ ($2.66 \pm 0.21\text{ kJ/mol}$) and the energy difference between the trans and gauche forms is $386 \pm 13\text{ cm}^{-1}$ ($4.61 \pm 0.16\text{ kJ/mol}$). Vibrational assignments have been made for the observed bands for the three conformers with initial predictions by MP2(full)/6-31G(d) ab initio calculations to obtain harmonic force constants, wavenumbers, infrared intensities, and Raman activities for the three conformers. By utilizing the microwave rotational constants of two isotopomers for trans, combined with the structural parameters predicted from MP2(full)/6-311+G(d,p) calculations, adjusted r_0 parameters have been obtained for the trans conformer. The results are discussed and compared to the corresponding properties of some related molecules.

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Introduction

Monofluoroacetic acid (FCH_2COX) derivatives are biologically renowned and they act in a toxic manner by disrupting the citric acid cycle in the human body [1]. Monofluoroacetic acid derivatives, mainly fluoroacetic chloride and fluoroacetic bromide, have

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been of interest for several decades and a number of researchers have studied the conformations of both these halides using vibrational spectroscopy. Many of the initial investigators utilized both infrared and Raman spectra for the conformational determination [2–7] and from these studies the trans form (Fig. 1) was assigned as the stable conformer. Additional investigations were carried out by microwave [8] and normal coordinate analysis [5] studies and these investigators established that the trans form is the more stable conformer for fluoroacetyl chloride. The rotational constants along with nuclear quadrupole coupling constants for the ground state were obtained from this study for the ^{35}Cl and ^{37}Cl isotopologues. The rotational constants of both the ^{35}Cl and ^{37}Cl isotopes were determined to be within ± 4 MHz.

The second most stable conformer for fluoroacetyl chloride was proposed by two investigators [8] to be the cis form. The presence of the high energy conformer as the cis form was demonstrated by Durig and coworkers [2] by utilizing vibrational studies. We have previously determined [2] the enthalpy differences between the two stable forms (trans and cis) of fluoroacetyl chloride by variable temperature studies of the Raman spectra from which the values of $509 \pm 37 \text{ cm}^{-1}$ ($1.46 \pm 0.10 \text{ kcal/mol}$) was obtained. However a much smaller value of $310 \pm 8 \text{ cm}^{-1}$ ($0.89 \pm 0.02 \text{ kcal/mol}$) was obtained from the variable temperature Raman spectra of the liquid, with the trans conformer as the more stable form. This study was followed by a variable temperature investigation carried out by Klaeboe [6] and co-workers by utilizing the Raman spectra of the liquid which gave a value of $518 \pm 33 \text{ cm}^{-1}$ as the enthalpy difference between the trans and gauche conformers. These results [2,6,8] were based on Raman spectra of variable temperature gas and liquid solutions, infrared spectra of the liquid and solid, and the microwave spectrum along with support by ab initio Hartree–Fock calculations. It is interesting to note that the above results were supported by a later low temperature xenon matrix study [3] from which it was determined that the gauche form was the high energy conformer. In this study the FT-IR spectrum of fluoroacetyl chloride trapped in a low temperature xenon matrix was recorded and the sensitivity of the sample to thermal effects and exposure to UV sources were analyzed. The high energy conformer was characterized by using the normal coordinate analysis method which was supported with ab initio force field calculations employing the 3-21 G basis set.

Therefore it is desirable to obtain more accurate enthalpy difference between the three conformers and obtain more precise structural parameters for fluoroacetyl chloride, so as to compare them to the previous fluoroacetyl chloride parameters. Thus we have investigated the vibrational spectrum of fluoroacetyl chloride with a study of the infrared spectra of the gas and solid. Additionally we have investigated the Raman spectra of the liquid as well as both the Raman and IR spectra of the variable temperature xenon solutions. To supplement the vibrational study, we have carried out ab initio calculations with basis sets up to aug-cc-pVTZ as well as those with diffuse functions, i.e., 6-311+G (2df,2pd). We have also carried out density functional theory (DFT) calculations by the B3LYP method with the same basis sets. We have calculated optimized geometries, conformational stabilities, harmonic force fields, infrared intensities, Raman activities and depolarization

ratios. The results of these spectroscopic, structural, and theoretical studies are reported herein.

Experimental methods

The sample of fluoroacetyl chloride with 97% purity was purchased from Alfa Products, Danvers, MA. The sample was further purified by low-temperature, low-pressure fractional distillation column. The purity of the sample was checked and verified by the infrared spectra.

Microwave spectra of fluoroacetyl chloride were recorded on a “mini-cavity” Fourier-transform microwave spectrometer [9,10] at Kent State University. The Fabry–Perot resonant cavity is established by two 7.5-inch diameter diamond-tip finished aluminum mirrors with a 30.5-cm spherical radius. The Fabry–Perot cavity resides inside a vacuum chamber formed by a 6-way cross and a 15-inch long, 8-inch diameter extension tube. One of the cavity mirrors is formed on an 8-inch diameter vacuum flange and mounted on the 6-way cross. The second mirror is mounted on 0.75-inch diameter steel rails that pass through ball bearing brackets mounted inside the extension arm. A motorized micrometer is used to position the movable mirror over a two-inch travel range. The two cavity mirrors are nominally separated by 30 cm. The vacuum chamber is pumped by a Varian VHS-6 diffusion pump (2400 L s^{-1}) backed by a two-stage Edwards E2M30 rotary pump.

The fluoroacetyl chloride sample was entrained in 70:30 Ne–He carrier gas mixtures at a pressure of 2 atm and expanded into the cavity with a reservoir nozzle [10] made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange which is external to the vacuum chamber and the expansion passes through a 0.182-inch diameter hole into the resonant cavity. The center of the expansion is offset from the center of the mirror by 1 inch.

The sample was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer and details of the irradiation and heterodyne detection circuitry can be found in Reference [11]. Labview software controls the timing of the gas and irradiation pulses, as well as the detection of any free induction decay signal. The software performs signal averaging and can scan the spectrometer by stepping both the frequency source and the cavity. Microwave circuit elements allow for a spectral range from 10.5 to 26 GHz. The digital frequency resolution is 2.5 kHz and governed by the sampling rate and by the length of the free induction decay record. Rotational transitions are split into Doppler doublets by typically 13 kHz centered at the transition frequency due to the coaxial orientation of the gas expansion to the cavity axis and the FWHM of each Doppler component. The assigned microwave lines are listed in Tables 1 and 2 and the rotational and centrifugal distortion constants are listed in Table 3.

The mid-infrared spectrum of the gas (Fig. 2A) and solid were obtained from 4000 to 220 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectra of the gas and solid were obtained with a theoretical resolution of 0.5 cm^{-1} for the gas and 2 cm^{-1} for the solid with 128 interferograms added and truncated.

The mid-infrared spectra ($3600\text{--}400 \text{ cm}^{-1}$) of the sample dissolved in liquefied xenon (Fig. 3B) were recorded at four different temperatures (-70 to $-100 \text{ }^\circ\text{C}$) on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the

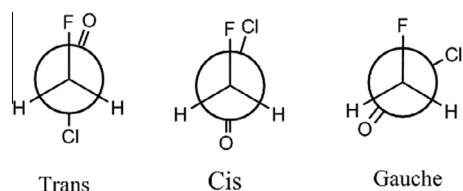


Fig. 1. Trans, Cis and Gauche conformers of fluoroacetyl chloride.

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