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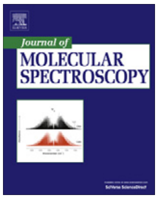

Calculated and experimental rotational spectra of 3,3,3-trifluoro- and 2,2,3,3-tetrafluoropropionyl chloride

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ABSTRACT

Quantum chemical calculations have been performed on the potential energy surfaces of the two title molecules. The calculations have located the two lowest energy conformations for each molecule. For all four structures, centrifugal distortion constants and chlorine nuclear quadrupole coupling tensor components have been calculated. Analyses of the experimental rotational spectra have yielded the identification of only one conformer for each molecule. These conformers have spectroscopic constants closely matching those of the calculated lowest energy conformers. The chlorine nuclear quadrupole coupling tensor components of the title molecules have been compared with those for propionyl chloride and perfluoropropionyl chloride.

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1. Introduction

Chirped pulse Fourier transform rotational spectroscopy is a useful tool in the physical sciences [1–4]. Amongst other uses, we have found the technique particularly useful in regards to structural characterizations for (i) exotic and/or transient species [5] and (ii) studies in which dense spectra occur [6]. In the former case, the broadband nature of the technique eliminates time consuming spectral searches allowing the focus of the study to be the synthetic component. In the latter case, the spectra generated have meaningful intensity information, which is of great use in quantum number assignments. Quantum number assignments are further facilitated through the ability to view large regions of spectra as a whole. However, dense spectra, whether they come from large molecules [7], mixtures of compounds [8], or conformationally complex species [9,10], especially when coupled with further complications such as hyperfine structure [11,12] or an internal rotor [13] (or both [14]) remain a challenging assignment problem. Quantum chemical calculations have become established as valuable tools in assisting with these tasks.

This work concerns the first rotational spectroscopy of 3,3,3-trifluoropropionyl chloride and 2,2,3,3-tetrafluoropropionyl chloride. These molecules may exist in multiple conformations, possess a hyperfine structure-generating nucleus, i.e. ^{35}Cl and ^{37}Cl ($I = 3/2$), and are both relatively heavy molecules (146.5 u and 164.5 u, respectively). Taken together, a reasonably dense spectra is anticipated and quantum chemical calculations are helpful for spectral assignment.

The molecules are of interest in regards to the geometric and electronic structural changes that occur in small functionalized organic molecules following the process of partial or complete fluorination. We have recently performed microwave spectroscopic studies on propionyl chloride and perfluoropropionyl chloride [15]. The title molecules of this study serve as partially fluorinated subjects within the same class of compound.

2. Experimental

In all experiments 3,3,3-trifluoropropionyl chloride (b.p. 344–345 K) and 2,2,3,3-tetrafluoropropionyl chloride (b.p. 311–313 K), were purchased from Synquest Labs, Inc., <97%, and were used separately without further purification. All experiments were performed at the University of North Texas. Each compound was handled in the same way. Approximately 5 ml of the liquid was placed 40 cm upstream of a solenoid valve in a 1/4 in. teflon tube. This tube was pressurized to 2 atm with argon gas. The solenoid valve was opened for 200 μs twice every second, therefore issuing a pulse of argon saturated with the target compound. The output of the valve was aimed toward a region of space located between two broadband microwave horn antennae housed within a vacuum chamber held at approximately 7 $\times 10^{-5}$ atm. The disparity

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between the argon stagnation pressure and vacuum chamber pressure caused the gas phase solution to undergo a supersonic expansion thus achieving rotational temperatures on the order of 4 K. Once located between the broadband horn antennae, one antenna is used to broadcast a fast linear frequency sweep, or chirp, of microwave radiation spanning 2 GHz in 6 µs. This "chirped" pulse of radiation is prepared using microwave circuitry described in detail in Ref. [4,15]. At the end of the microwave broadcast the reception of molecular signals begins through the second horn antenna. The signal received is generated by the ensemble of target molecules as they undergo decoherence from a macroscopically polarized state induced through resonance of pure rotational transitions with microwave frequencies contained within the microwave pulse. The molecular signal is amplified and then digitized on a broadband oscilloscope as a free induction decay at a rate of 40 gigasamples per second. Twenty microseconds of the time diminishing waveform is then fast Fourier transformed to produce a power spectrum displaying the discrete frequencies of each rotational transition. These experiments were repeated 30,000 times, with the results averaged together in order to improve the signal to noise ratio of collected spectra. The frequency region of 8–14 GHz was covered in three 2 GHz steps.

The spectral line widths obtained with this technique are approximately 80 kHz full width at half maximum height, and an uncertainty of 8 kHz is attributed to unblended spectral transition measurements.

3. Theoretical

Quantum chemical calculations were performed for each title molecule to provide (i) molecular structures of the lowest energy conformers to assist with quantum number assignments, (ii) estimates of inertial axes nuclear quadrupole coupling components to assist with hyperfine structure assignment and (iii) estimates of rotational constants, centrifugal distortion constants, and relative dipole moment components. All calculations were performed using the Gaussian 03 suite of programs [16].

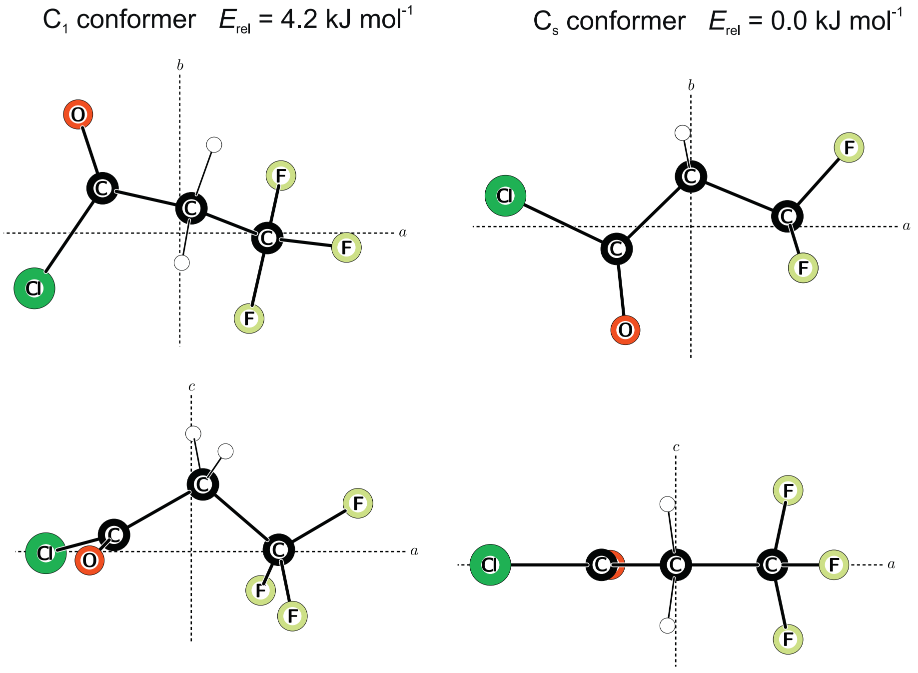
Computational strategies adopted here are described in detail in a previous publication concerning the similar molecule, chlorodifluoroacetyl chloride [12]. In brief, approximate equilibrium structures are derived by MP2/aug-cc-pVTZ optimization, followed by empirical correction of the optimized bond lengths. Two minimum energy conformers have been identified for each molecule, C_s and C_1, as shown in Figs. 1 and 2. For $CF_3CH_2C(=O)$ Cl, E $(C_s) <$ E (C_1) by about 4.2 kJ/mole; whereas for $CHF_2CF_2C(=O)Cl$, E $(C_1) <$ E (C_s) by about 0.2 kJ/mole. In Tables 1 and 2, common C–C–C(=O)–Cl structure parameters for these are compared.

On these structures, electric field gradient components q_{ij} were calculated at the B1LYP/TZV (3df, 2p) level of theory, and converted to NQCC components χ_{ij} by means of $eQ/h(^{35}Cl) = -19.185$ MHz/a.u. and $eQ/h(^{37}Cl) = -15.120$ MHz/a.u in the following equation:

$$\chi_{ij}(\text{MHz}) = (eQ/h) \times q_{ij}(\text{a.u.}), \qquad (1)$$

where e is the fundamental electric charge, Q is the electric quadrupole moment of the nucleus in question, and h is Planck's constant. The conversion factors eQ/h given above are derived with $Q(^{35}Cl) = -81.65(80)$ mb and $Q(^{37}Cl) = -64.35(64)$ mb [17]. B1LYP is Becke's one-parameter method with Lee–Yang–Parr correlation as implemented by Adamo and Barone [18,19]. TZV are Ahlrichs bases [20] augmented here with three sets of d and one set of f polarization functions on heavy atoms, and two sets of p functions on hydrogens [12,21].

Inertial axes χ_{ij} thus calculated are given in Table 3 (3,3,3-trifluoropropionyl chloride) and Table 4 (2,2,3,3-tetrafluoropropionyl chloride), along with calculated rotational constants, quartic centrifugal distortion constants, and B1LYP/TZV (3df, 2p) calculated dipole moment components. Quartic centrifugal distortion constants were calculated at the B3LYP/cc-pVTZ level of theory, where B3LYP is Becke's three-parameter with Lee–Yang–Parr correlation [22] and cc-pVTZ are Dunning bases [23]. This methodology has been shown to produce accurate force fields at low cost [24].


C_1 conformer $E_{rel} = 4.2$ kJ mol^{-1}

C_s conformer $E_{rel} = 0.0$ kJ mol^{-1}

Fig. 1. Calculated structures of the two lowest energy conformers of 3,3,3-trifluoropropionyl chloride in the *ab* and *ac* planes.

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