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# The structure and helicity of perfluorooctanonitrile, $CF_3$–$(CF_2)_6$–CN

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## ABSTRACT

New molecular structural data is presented for a cyanide terminated oligomer of polytetrafluoroethene. The target molecule, $CF_3$–$(CF_2)_6$–CN, has been seeded within a pulsed supersonic expansion of argon. The result of this action is to cool the species to rotational temperatures below 4 K. Within this state, the pure rotational spectrum of the oligomer has been recorded using two types of Fourier transform microwave spectroscopy. A total of 111 transitions have been identified involving rotational $J$ levels between 6 and 40. Only $a$- and $b$-type transitions were observed. The spectrum has been analyzed using a Hamiltonian containing all three rotational constants and one centrifugal distortion constant, $D_J$. The experimental spectroscopic constants have been used to develop an effective molecular structure by scaling the quantum chemical calculated structure. The data shows that the seven carbon perfluorinated chain for the isolated oligomer twists ≈104°. This compares well to the $C_7F_{13}$-twist of ≈97° anticipated from the X-ray structure of phase II polytetrafluoroethene.

## 1. Introduction

A famous, fortuitous accident lead to the discovery of polytetrafluoroethene, PTFE, by Plunkett in 1938 [1]. In 1954, Bunn and Howells [2] recorded X-ray diffraction photographs of drawn fibers of PTFE below 19 °C. From these photographs a chain repeat-distance was determined to be 16.8 Å. The photographs further revealed a reflection from a plane perpendicular to the chain axis with a Bragg spacing of 1.294 Å, one thirteenth of the chain repeat. This finding is explained by a plane zig-zag structure which twists 180° in 13 carbon atoms. A full 360° twist of the chain occurs in 26 carbon atoms, but the actual period is one half this because the zig-zag structure consists of two rows of carbon atoms and one 180° twist brings the fourteenth carbon in the second row to be just above the first carbon in the first row.

A recent review by Yashima [3] discusses the importance of helical polymer synthesis in regards to enantiomeric separations and asymmetric catalysis, and goes on to discuss the difficulties associated with structural determinations. Powerful structural tools discussed in that review include single crystal and liquid crystal X-ray diffraction, circular dichroism, and also atomic force microscopy. These tools focus on unit cell or "generic" structural parameters, rather than focusing on molecular structural details.

Implicit in a recent study by Fournier et al. [4] is a novel, "bottom up" approach to polymer structure determinations. In this approach, high resolution rotational spectroscopy augmented with accurate quantum chemical calculations is used to provide detailed structural information on proto-type oligomeric units.

In this paper we further demonstrate the use of rotational spectroscopy in regards to the structural determinations of oligomers. A fundamental study of the perfluoro helix in PTFE is the subject of this work.

Several important "bottom up" carbon chain lengths are important in the structural evolution of PTFE. The first question concerns the chain length required for helicity to manifest. Fournier et al. [4] have answered this question using experimental data from the $C_3$ and $C_5$ systems. A four carbon chain is required for a helical structure. Further chain lengths of interest include the 7, 13, and 26 carbon species as these lengths should be sufficient to exhibit one quarter, one half, and one full helical twist, respectively.

Following Fournier et al. we have employed a "bottom up" rotational spectroscopy approach to characterize an oligomer containing a perfluorinated eight carbon chain. Rotational spectroscopy requires that the target species possess a dipole moment. In order to increase the dipole moment of $C_7F_{15}$– we have studied a species with a terminal –CN group. This group may be considered a "polar-o-phore", in analogy to the addition of a chromophore in ultra-violet/visible spectroscopy.

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## 2. Methods

### 2.1. Experimental

In this work we propose the use of Fourier transform microwave spectroscopy as an experimental method useful for oligomer and polymer structural determinations. Below, we briefly present the experimental method, however, greater detail may be found in many recent reviews. See for example Refs. [5–7].

In all experiments, perfluorooctanonitrile (Synquest Labs, Inc., 99%, Bp. 373–374 K at 705 mm Hg) was used without further purification. 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 once every second, therefore issuing a pulse of argon saturated with perfluorooctanonitrile. 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 between the argon stagnation pressure and vacuum chamber pressure caused the perfluorooctanonitrile/argon gas phase solution to undergo a supersonic expansion thus achieving rotational temperatures on the order of 4 K. 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. [8]. 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 perfluorooctanonitrile 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, or $2.7 \times 10^{-6}$ cm$^{-1}$, full width at half maximum height, and an uncertainty of 8 kHz applies to unblended spectral transition measurements.

Certain spectral features were investigated using a similar technique in which the horn antennae are replaced by two opposing mirrors, forming a microwave cavity, with 1/4 wavelength dipole antennae located at the mirror centers. In this configuration, monochromatic microwave frequencies are used. One mirror is movable, and the separation between the mirrors is adjusted to form a standing wave at the frequency of interest. The high quality of the cavity, coupled with the monochromatic source, results in only 0.5 MHz portions of spectra being observable in any one experiment. This technique is explained in greater detail by its inventors in Ref. [9]. The locally used instrument has been presented in Ref. [10]. This mirror, or cavity, technique provides a convenient way to "zoom in" on spectral transitions previously located with the chirped pulse technique described above. With the cavity arrangement unblended spectral line widths of 7 kHz are easily achievable. When using the cavity technique transitions are observed as Doppler doublets owing to the molecular source being coaxial with the direction of microwave propagation. In the chirped pulse arrangement the molecular source is perpendicular to the direction of microwave propagation and Doppling doubling does not occur.

### 2.2. Quantum chemical calculations

Perfluorooctanonitrile contains 24 atoms and 190 electrons. Furthermore, the molecule has no symmetry and possesses many structural degrees of freedom. These factors combine to make *ab initio* calculations time consuming.

Instead a density functional theory approach with the hybrid PBE0 functional was used [11–13] together with the aug-cc-pVTZ basis set for all atoms [14,15]. This functional has been shown to perform well with perfluorinated systems [16]. Calculations were performed using the Gaussian 03 suite of software [17]. In order to anticipate the effect on the observed spectra of the coupling of angular momenta from the quadrupolar nitrogen nucleus and the end-over-end rotation of the molecule, values of the elements of the nitrogen nuclear electric quadrupole coupling tensor were calculated. Effects such as these are common in nuclear magnetic resonance spectroscopy and are often observed in microwave spectra. This calculation was performed at the B3PW91 level of theory [18,19] in conjunction with Pople 6-311+G(df,pd) bases. Electric field gradient components $q_{ij}$ thus calculated were converted to nuclear quadrupole coupling constant components $\chi_{ij}$ via $eQ/h = 4.5586(40)$ MHz/a.u. in $\chi_{ij} = (eQ/h)q_{ij}$ [20–23]. (A Fortran program for transformation of the $q_{ij}$ calculated in Gaussian 03 standard orientation coordinates to inertial axes coordinates is available in Ref. [21].)

## 3. Results

The recorded spectrum was weak. However, the observation of a repeating pattern of transitions every 250 MHz provided sufficient information to begin a successful quantum number assignment. A total of 111 rotational transitions were assigned and a listing of these data is presented in the Supplementary material. The transitions assigned were *a*-and *b*-types; no *c*-type transitions were observed consistent with the $C_7CN$ backbone lying mainly in the *ab* plane. No unassigned transitions were observed. A portion of the spectrum is shown in Fig. 1. The types of transitions observed were consistent with the molecule possessing a significant dipole along the *a* and *b* principal axes. Following the transition assignment, an iterative least squares fitting procedure [24] was undertaken in which the parameters of a suitably formed Hamiltonian operator were adjusted until the resulting calculated spectrum matched the observed spectrum to within experimental uncertainty. The only parameters required within the Hamiltonian were the three rotational constants, *A*,*B*, and *C*, and the leading quartic centrifugal distortion constant, $D_J$. The values of these constants are presented in Table 1 together with the rotational constants resulting from the DFT calculated structure. Nitrogen hyperfine splitting was not resolvable in these experiments. A predicted spectrum using the calculated nitrogen quadrupole coupling tensor, presented in Table 2, also shows the hyperfine splittings being less than the resolution of the spectrometers used.

The calculated structure, in all three principal planes, is presented in Fig. 2. The bond lengths, bond angles and dihedral angles for this structure are reported in Table 3.

## 4. Discussion

### 4.1. Oligomer structure

The rotational constants of a molecule are inversely proportional to the moments of inertia about the molecule's principal axes. The moments of inertia depend upon the molecular spatial distribution of atomic mass and therefore contain structural