Journal of Molecular Spectroscopy 266 (2011) 37–42

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

A chirped pulse Fourier transform microwave study of the refrigerant alternative 2,3,3,3-tetrafluoropropene

Mark D. Marshall [a],*, Helen O. Leung [a],*, Benjamin Q. Scheetz [a], Jonathan E. Thaler [a], John S. Muenter [b]

[a] Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000, United States
[b] Department of Chemistry, University of Rochester, Rochester, NY 14627, United States

ARTICLE INFO

Article history:
Received 21 January 2011
In revised form 11 February 2011
Available online 19 February 2011

Keywords:
Microwave spectroscopy
Refrigerant
Structure determination
Chirped pulse
HFO-1234yf

ABSTRACT

Fourier transform microwave, rotational spectra in the 6–18 GHz band of the low global warming potential, low ozone depletion potential refrigerant alternative, 2,3,3,3-tetrafluoropropene (HFO-1234yf), and in natural abundance, its three singly substituted ^{13}C isotopologues are obtained using a newly constructed chirped pulse spectrometer. Employing anharmonic vibration–rotation interaction alpha constants from *ab initio* calculations, the rotational constants determined for the ground vibrational state of the molecule are corrected to provide equilibrium values of these constants for all four isotopologues. The equilibrium constants are used for structure determination via both Kraitchman substitution coordinates and least squares fits to equilibrium moments of inertia. Both experiment and theory give a structure in which all but two fluorine atoms in the terminal $-CF_3$ group are coplanar. A substantial barrier to internal rotation of this group is predicted by *ab initio* calculation, and no evidence of internal rotation is seen in the spectra. A detailed description of the new spectrometer is given.

1. Introduction

The chirped pulse, Fourier transform microwave, CP-FTMW, spectroscopy technique recently developed by Brooks Pate and coworkers is a productive tool for studying structure, properties and dynamics of polar molecules that can be entrained in a supersonic expansion [1–7]. This paper presents initial results from a newly constructed CP-FTMW instrument at Amherst College.

Recently, we have been investigating the effects resulting from changes in the degree of fluorine substitution on the intermolecular interactions between fluoroethylenes and protic acids via microwave spectroscopic determination of the structures of the bimolecular complexes formed between these species. Building upon initial work from the Legon group, structures have been determined for the complexes formed between, on the one hand, hydrogen fluoride (HF), hydrogen chloride (HCl), and acetylene (HCCH) with vinyl fluoride [8–11], 1,1-difluoroethylene [12–14], and 1,1,2-trifluoroethylene [15–17] on the other. We have also determined the structure of the *trans*-1,2-difluoroethylene-HF complex [18]. Each of these complexes is planar and contains two non-covalent interactions: a primary, hydrogen bonding interaction between the protic acid and one of the fluorine atoms on the substituted ethylene, and a secondary interaction between a hydrogen atom in the substituted ethylene and the nucleophilic portion of the acid. This latter interaction is made possible by a deviation of the hydrogen bond from linearity. We have observed that an increase in the number of fluorine substituents has significant effects on the nature of the intermolecular interactions, causing not only changes in the specific values of the geometric parameters, but also a change in the mode of binding itself. We have interpreted these results in terms of the electronic distribution of the fluoroethylene monomer, which is influenced by the number of fluorine atoms it contains, and the importance of attaining a balance between electrostatic and steric effects [18].

We have recently extended this work to consider not only fluorine, but also chlorine substitution [19], and we also wish to investigate the effects of the increased degree of fluorine substitution that can occur in larger olefins. A complex formed between a protic acid and 2,3,3,3-tetrafluoropropene (TFP), when compared with the analogous vinyl fluoride or 1,1-difluoroethylene species, would show the consequences of replacing a hydrogen atom or a fluorine atom, respectively, by the $-CF_3$ moiety. It also provides fluorine atoms bonded to both sp^2 and sp^3 hybridized carbon atoms as well as the increased steric options made possible by the longer carbon backbone.

Additionally, TFP is itself an important molecule as it is likely to become the dominant refrigerant in automobile air conditioners [20]. Also known as HFO-1234yf, it is a “drop-in” replacement for the currently used 1,1,1,2 tetrafluoroethane, R-134a, which will be banned in Europe in 2011 because of its ozone destroying

---

* Corresponding authors. Fax: +1 413 542 2735.
E-mail addresses: mdmarshall@amherst.edu (M.D. Marshall), hleung@amherst.edu (H.O. Leung).

0022-2852/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2011.02.005

properties. The residence time of TFP in the atmosphere is approximately 1/400 that of R-134a and is not considered to affect atmospheric ozone concentrations [21]. With mass production of TFP ramping up, there are a variety of reasons for obtaining additional spectroscopic and structural information for this molecule.

We report here the 6–18 GHz microwave rotational spectrum of TFP and its singly substituted ^{13}C isotopologues (in natural abundance) obtained with our new CP-FTMW spectrometer. In combination with results from *ab initio* quantum chemical calculations including vibration–rotation interaction constants, we have determined several equilibrium structural parameters for this molecule.

2. Experimental

Since this paper contains the first results from a new spectrometer, we provide a somewhat detailed discussion of the apparatus. The Pate group has been extraordinarily generous in providing other researchers with the many details necessary for the construction of CP-FTMW spectrometers. The choices made to configure a specific instrument are frequently determined by budget considerations, and the most important criterion in this regard is the bandwidth of the chirped pulse. As the frequency range of the microwave pulse is increased, the spectral coverage available for each data acquisition increases correspondingly. However, broader chirp bandwidth significantly increases the cost of the three most expensive electronic components of the spectrometer: the arbitrary waveform generator, the signal digitizer, and the microwave power amplifier. We have chosen to cover the 6–18 GHz frequency range in two bands, 6–12 GHz and 12–18 GHz. Switching between these bands can be accomplished in a few minutes since only two components have to be changed, both of which are outside the vacuum chamber.

The block diagram for the instrument is shown in Fig. 1. Each of the 23 main components is numbered, and specific details, including manufacturers and part numbers, are available as Supplementary material. The pulsed valve (#5), microwave horns (#9), switch (#10) and preamplifier (#15) are contained in a stainless steel vacuum chamber roughly 90 cm × 50 cm × 30 cm (LWH) which is evacuated by a Varian VHS10 diffusion pump. While many of the microwave components are specified to cover the 6–18 GHz frequency range, and the nominal bandwidth of the microwave horns is 6.5–18 GHz, they can be used to considerably lower frequency with some reduction in sensitivity. The absolute lowest frequency limit of the spectrometer configuration is given by the 5.348 GHz cutoff frequency of the double ridged waveguide used in the horns. The lowest frequency transition used in this study occurs at 5.534 GHz.

The Tektronix 7101 arbitrary waveform generator (AWG, #13) uses a 10 GHz sampling rate and thus can produce pulses with frequency components up to 5 GHz. However, the output of the waveform generator also contains a strong 10 GHz clock signal that mixes with the primary, programmed chirp. Consequently, a programmed chirp of 0.5–5.0 GHz will also produce a sideband chirped signal of 10.0 – (0.5 to 5.0) = 9.5 to 5.0 GHz. These two chirps are processed with a low pass filter (#12) that rolls off the higher frequency content of the sideband signal leaving two chirps of 0.5–5.0 and 6.6–5.0 GHz [22]. These microwave pulses are mixed with the output of a phase locked dielectric resonator oscillator (PDRO, #23) in the double balanced mixer (#11), and the lower sideband is selected by a filter (#6). Specifically, for the lower frequency spectrometer band, extending from (nominally) 6.0–12.1 GHz, the PDRO frequency is 12.6 GHz and filter (#6) is a 12.0 GHz low pass filter. This combination produces two chirps, 6.0–7.6 GHz and 12.1–7.6 GHz. The higher frequency spectrometer band is accessed with an 18.6 GHz PDRO and a 12–18 GHz band pass filter. In this case the two chirps extend from 18.1 to 13.6 GHz and from 12.0 to 13.6 GHz.

The output of filter #6 is amplified (#7), sent to a gated power amplifier (#8) and then to the input horn (#9) which broadcasts the radiation used to polarize the sample. The free induction decay (FID) signal emitted by the polarized molecules is collected by the second antenna horn, passed through a switch (#10) that blocks the polarizing microwave pulse from the low noise preamplifier (#15), further amplified (#21), down converted by a mixer (#22) using the same PDRO signal as local oscillator, and sent to be

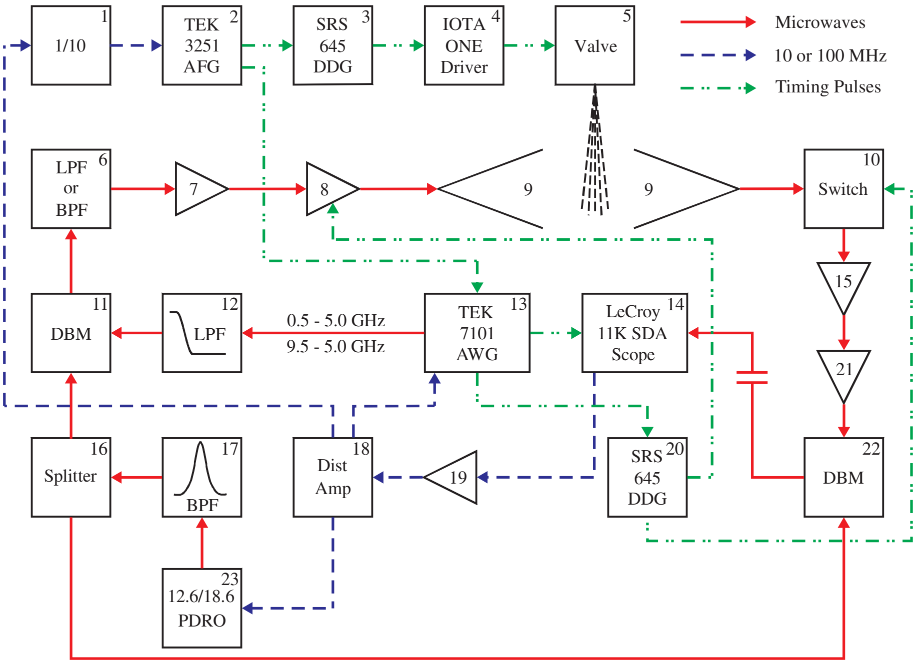

Fig. 1. Block diagram for the chirped pulse microwave spectrometer. See text for more information on each component. Manufacturers and part numbers for the numbered components are listed in Supplementary material.