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A K_a-band chirped-pulse Fourier transform microwave spectrometer

Daniel P. Zaleski [a], Justin L. Neill [a], Matt T. Muckle [a], Nathan A. Seifert [a], P. Brandon Carroll [b], Susanna L. Widicus Weaver [b,*], Brooks H. Pate [a,*]

[a] Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904, USA
[b] Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 3032, USA

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ABSTRACT

The design and performance of a new chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer operating from 25 to 40 GHz (K_a-band) is presented. This spectrometer is well-suited for the study of complex organic molecules of astronomical interest in the size range of 6–10 atoms that have strong rotational transitions in K_a-band under pulsed jet sample conditions (T_{rot} = 1–10 K). The spectrometer permits acquisition of the full spectral band in a single data acquisition event. Sensitivity is enhanced by using two pulsed jet sources and acquiring 10 broadband measurements for each sample injection cycle. The spectrometer performance is benchmarked by measuring the pure rotational spectrum of several isotopologues of acetaldehyde in natural abundance. The rotational spectra of the singly substituted ^{13}C and ^{18}O isotopologues of the two lowest energy conformers of ethyl formate have been analyzed and the resulting substitution structures for these conformers are compared to electronic structure theory calculations.

1. Introduction

Chirped-pulse Fourier transform microwave (CP-FTMW) spectrometers provide instantaneous broadband spectral coverage for measurement of molecular rotational spectra [1]. The sensitivity of the spectrometer can be enhanced by using multiple pulsed jet sources to increase the number of molecules in the active volume and by acquiring multiple spectra for each sample injection cycle. These broadband spectrometers offer complementary performance to narrowband cavity FTMW spectrometers – based on the Balle–Flygare design [2]. The CP-FTMW design is best suited for applications that require a survey spectrum of a sample with an unknown composition. The mixture can include a variety of distinct chemical species or several isomers (conformational or isotopologues) of a single species. In these applications, the key advantages of CP-FTMW spectrometers are accurate relative intensities across the measurement band, shorter measurement time in acquiring a broad-bandwidth spectrum (in part from the simplified operation requiring no mechanical repositioning of cavity mirrors), and the ability to use multiple pulsed jet sources in the free space interaction region to minimize sample consumption and measurement time to reach a target sensitivity. In contrast, the passive gains inside the microwave cavity achieved in Balle–Flygare spectrometers are better suited for applications where a single transition is monitored since optimal excitation conditions can routinely be achieved with the power available from standard microwave components. The passive gain may also give an advantage to Balle–Flygare spectrometers for studies of molecules with small dipole moments and may be particularly important in the K_a-band frequency region that is the focus of this work because the microwave power amplifiers required for CP-FTMW spectroscopy provide relatively low power (about 40 W compared to 300 W or more for frequencies below 18 GHz). The cavity FTMW spectrometers are also well suited to limited search applications where an accurate prediction of the spectrum for the species of interest is available. During the past few years, the applications of chirped-pulse spectroscopy have been numerous, including the study of metal-containing molecules [3–6], conformationally rich molecules [7], and molecular clusters [8]. Chirped-pulse instruments have also been developed to work over reduced bandwidths and at low frequency [9,10].

Recently, the CP-FTMW technique has been extended to mm-wave operation. The Field group at MIT has constructed a chirped-pulse millimeter-wave spectrometer (CP-mmW) operating between 70–84 GHz and 87–102 GHz and applied it to studies of molecules produced in electric discharge sources [11] and the spectroscopy of atomic Rydberg states prepared by laser [12]. The operation of CP-FT spectrometers at frequencies up to about 1 THz has been demonstrated at NIST [13]. Both of these high-frequency spectrometers have used solid-state frequency multiplier devices to generate the chirped-excitation pulse. Despite the relatively low peak powers of these sources (<100 mW) both of

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* Corresponding authors.
E-mail addresses: susanna.widicus.weaver@emory.edu (S.L. Widicus Weaver), bp2k@virginia.edu (B.H. Pate).

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these spectrometers have demonstrated high measurement sensitivity.

The extension of CP-FTMW techniques to mm-wave and THz frequency ranges is expected to impact spectroscopic studies of molecules with astrochemical importance. A new generation of radio astronomy interferometers that combine broadband spectral detection with high spatial resolution have commenced science operations in the past 2 years. The Jansky Very Large Array (JVLA) operates in the microwave frequency range (up to 50 GHz), and the Atacama Large Millimeter/Sub-millimeter Array (ALMA) has the potential for mm-wave spectral coverage in all atmospheric windows up to 1 THz. These facilities will produce about 1 PB/yr of spatially-resolved high-resolution interstellar molecular rotational spectra. Science verification data demonstrating the capabilities of ALMA have recently been made publicly available [14]. With the improved detection sensitivity and spatial resolution of next generation radio astronomy observatories, it is reasonable to expect that the amount of unassigned astronomical spectral data will increase rapidly. For a typical astronomical survey [15], there are already more unassigned transitions than known transitions. Since the rotational spectra of most readily available molecules are known, the remaining unknown transitions are likely novel species including high energy isomers, molecular ions, radicals, and vibrationally excited states that are populated in the hot core star-forming regions of interstellar clouds, where the organic chemistry becomes complex. CP-FTMW spectrometers are compatible with pulsed molecular beam sources, like electric discharge sources, that are capable of producing short-lived non-terrestrial species (e.g. ions, radicals, and high energy isomers) in sufficient quantities for spectroscopic analysis [16–21]. In particular, the combination of high spectral resolution, measurement dynamic range, and rotational cooling of pulsed jet spectrometers for rotational spectroscopy facilitate the analysis of the complex sample mixtures produced by reactive chemistry sources.

Here we demonstrate the operation of a K_a-band (26–40 GHz) CP-FTMW spectrometer. The spectrometer design is based on previous spectrometers operating below 18 GHz [1] and uses a pulsed traveling wave tube amplifier to achieve efficient sample excitation. This frequency range is well-suited to the study of molecules of astrochemical interest, typically containing 7 or fewer non-hydrogen atoms, because the peak intensity of their rotational spectra often fall in the K_a-band frequency range under molecular beam conditions (T_{rot} = 1–10 K). This instrument builds on technological advances in arbitrary waveform generation that is commonly used for telecommunications. Such an instrument will help unite laboratory spectroscopy with radio astronomical measurements and, in particular, provides direct spectral overlap with the National Radio Astronomy Observatory Green Bank Telescope (GBT) and JVLA. This new spectrometer facilitates the study of molecules relevant to astrochemistry with the spectral simplification of a pulsed-jet source.

2. Experimental

A schematic of the K_a-band CP-FTMW spectrometer is shown in Fig. 1. A 24 GS/s arbitrary waveform generator (AWG) (Tektronix AWG7122B) creates a 1 μs linear frequency sweep (chirped pulse) covering the frequency range from 10.5 to 3 GHz. A 12.2 GHz low-pass filter is used on the output of the AWG to filter out high frequency components that are produced by the mixing of the primary sweep with the AWG clock frequency. The chirped pulse is up-converted using a triple-balanced mixer (Miteq TB0440LW1) and a 23 GHz local oscillator (Microwave Dynamics, PLO-4070-23.00). This local oscillator is a 23 GHz phase-locked dielectric oscillator (PDRO) that has its output filtered by a 6-pole cavity bandpass filter (K&L Microwave, 6C62-23000/T100-K/K) to improve spectral purity. The lower frequency sideband from this mixing stage, with a frequency range of 12.5–20 GHz, is used to generate the final chirped-pulse after frequency doubling. In this design, the active frequency doubler (Wright Technologies, 100 mW output power, ATX40-220) accepts input frequencies from about 13–20 GHz with a sharp fall off in doubling efficiency above 20 GHz input frequency. Therefore, this device also serves to filter out the upper sideband of the mixing stage (26–33.5 GHz). The microwave pulse is amplified (Miteq, JS4-12002600-25-5P, 12–26 GHz bandwidth) to 10 mW prior to being input to the active frequency doubler. The frequency-doubled output is filtered by a nominal 26–40 GHz bandpass filter (Microwave Circuits, Inc., H26G40G1) and attenuated to 1 mW peak power for input to the K_a-band power amplifier. Fig. 2 shows a spectrogram of the chirped pulse at this stage. In addition to the primary pulse, spurious chirps due to sub-harmonic mixing are observed and are approximately 20 dB weaker than the primary chirp.

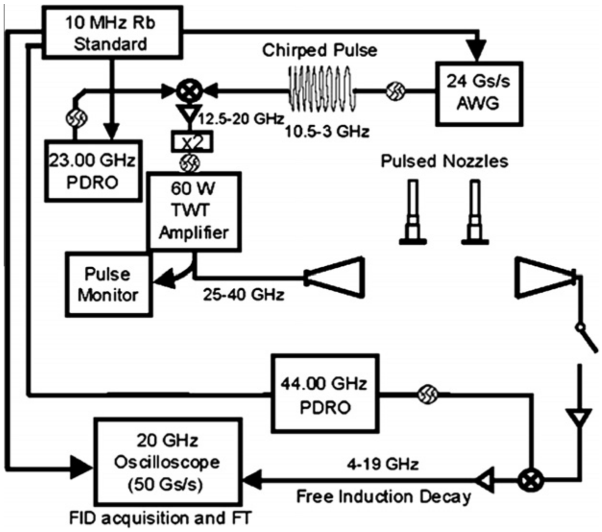

Fig. 1. Schematic of the K_a-band CP-FTMW spectrometer.

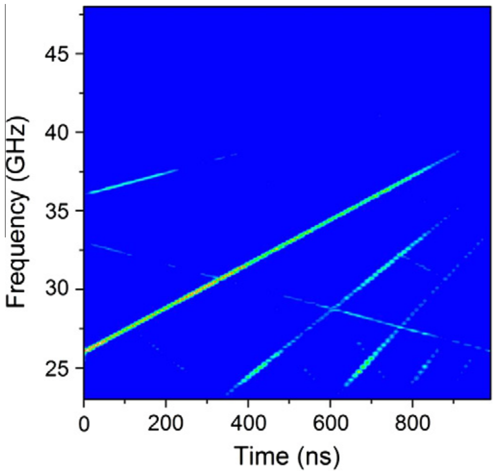

Fig. 2. A spectrogram of the microwave pulse before entering the TWTA. The effects of sub-harmonic mixing and additional outputs of the doubler can be seen.

The K_a-band chirped pulse is input into a pulsed traveling wave tube amplifier (TWTA, Applied Systems Engineering, 187Ka 105304-1) which has a measured output of 60 W mid-band with power output of greater than 40 W across K_a-band. This amplifier