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Chirped-pulse microwave spectrum and *ab initio* calculations of four distinct conformers of 3-vinylbenzaldehyde

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ABSTRACT

Chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy was used to measure the pure rotational spectrum of 3-vinylbenzaldehyde (3VBA) in four distinct conformations in the 8–18.5 GHz region of the microwave spectrum. The rotational constants and centrifugal distortion constants of each conformer were determined and compared with the supporting *ab initio* calculations performed at the Hartree–Fock, DFT, and MP2 levels of theory. Details of the CP-FTMW spectrometer are also discussed.

1. Introduction

3-vinylbenzaldehyde (3VBA, $C_2H_3C_6H_4COH$) is a cyclic organic compound used in many polymer and biochemical syntheses. 3VBA has been used in the synthesis of polymeric nitrons [1], de-cross-linking polymer systems [2], block copolymers [3,4], tethered phosphinoarene–ruthenium dichlorides [5], and Src kinase inhibitors [6]. 3VBA has also proved useful in the surface immobilization of oligonucleotides [7], and the synthesis of patterned superhydrophobic–superhydrophilic surfaces [8]. In this study, the measurement and analysis of the microwave spectrum of 3VBA is presented; to our knowledge, this work represents the first spectroscopic study of this molecule.

3VBA has two independent groups (the aldehyde group and the vinyl group) that can rotate about their axes with respect to the benzene group. These permutations result in four distinct energy minima, the structures and labels of which are shown in Fig. 1. The conformers are labeled *trans*, *cis*; *trans*, *trans*; *cis*, *cis*; *and cis*, *trans*, where the first label refers to the position of the oxygen atom relative to the vinyl group, and the second label refers to the position of the carbon–carbon double-bond relative to the aldehyde group. Due to the oxygen atom in the aldehyde group, all four conformers have a significant dipole moment. The presence of multiple polar conformers results in a rich pure rotational spectrum with which to test new instrumentation.

The CP-FTMW spectrometer used in this study is based upon a design developed in the Pate laboratory, which covered 11 GHz (7.5–18.5 GHz) with each chirped microwave pulse [9]. Using a similar design, the Cooke laboratory developed a spectrometer capable of measuring 4 GHz bandwidth with each pulse [10]. A less expensive, lower bandwidth 480 MHz CP-FTMW was subsequently developed in the Peebles laboratory [11]. Recently, the Blake group reported a CP-FTMW spectrometer that further reduced the cost of the instrumentation by employing a direct digital synthesizer (DDS) to generate a chirped pulse in place of an arbitrary waveform generator [12]. In this paper, we present a spectrometer similar in bandwidth to the Peebles' spectrometer. The decrease in bandwidth lowers the cost (compared to the Pate design) of the digital electronics by approximately an order of magnitude. Similarly, it decreases the cost of the power amplifier, as less power is required to effectively polarize a narrower bandwidth. However, the tradeoff of narrower bandwidth is an increased acquisition time for measurement relative to the full 8–18.5 GHz bandwidth, as the spectrum must now be acquired in smaller segments and concatenated together. Other differences from the Pate design (and the Peebles design) include a pulsed valve that is coaxial with respect to the microwave radiation and the use of a single horn in conjunction with a stationary, spherical mirror. This instrumentation is described in greater detail below.

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2. Experimental

2.1. Instrument design

A diagram of the spectrometer is shown in Fig. 2. It employs an arbitrary function generator (Tektronix AFG3252) to generate a 1 μs long, 250 MHz chirped pulse (linear frequency sweep from DC to 250 MHz). This instrument has a nominal hardware bandwidth of 240 MHz (2 GS/s digitizer rate), but for this study it has been used up to 250 MHz without noticeable problems. The chirped pulse is mixed (Miteq DM0520LW1 mixer) with a carrier frequency (ν_0) produced by a microwave signal generator (Hewlett Packard 8341A, 0.01–20 GHz). The resulting microwave pulse includes both sidebands of the mixer; thus, it covers the frequency range from ν_0 to 250 MHz to ν_0 + 250 MHz. The 500 MHz chirped pulse is amplified by a 1 Watt solid state amplifier (Microwave Power L0618-30, 6–18 GHz) and then broadcast into the high-vacuum chamber by a microwave horn antenna (Advanced Technical Materials 750-442-C3, 7.5 – 18 GHz), which employs a mica window (SPI Supplies 01872-CA) to maintain the vacuum. Facing the horn antenna is a stationary, spherical aluminum mirror with a radius of curvature of 30 inches; the mirror is approximately 32 inches from the microwave antenna. Gas is introduced into the chamber by a pulsed valve (General Valve Series 9, 1 mm orifice), which is mounted outside the vacuum chamber and expands through a small hole in the center of the mirror. Thus, each microwave pulse interacts with the molecular sample once before and once after reflection from the mirror. After the chirped pulse polarizes the molecular sample, a free induction decay (FID) is collected by the same horn antenna, passes through a circulator (TRAK Microwave 50A2061), a diode limiter (Advance Control Components, ACLM-4619FC36), and a low-noise amplifier (LNA, Miteq AMF-5F-06001800–15-10P, 1.5 dB noise figure, 6–18 GHz). The diode limiter is placed in the circuit before the LNA to protect it from the high-powered microwave pulse. Finally, the resulting FID is down-converted by mixing (Miteq DM0520LW1) with the same carrier frequency (ν_0) used to up-convert the linear chirp. After down-conversion, the FID is amplified again (Minicircuits ZFL-1000LN+, DC – 1 GHz) and digitized on a digital oscilloscope (Tektronix DPO7104, 1 GHz, 20 GS/s).

Since the down-conversion of the FID uses the same carrier frequency as the up-conversion of the chirped pulse, it is necessary to perform two measurements to determine the absolute frequency of a molecular signal. To accomplish this task, the spectrum is recorded in 250 MHz steps, and each frequency segment is compared with the two adjacent segments. If a peak is observed at the same absolute frequency in two overlapping segments (e.g. a molecular frequency of 11099 MHz would be down-converted to 99 MHz for ν_0 = 11000 MHz and 151 MHz for ν_0 = 11250 MHz), the molecular frequency is determined. In the present experiment, the 8–18.5 GHz spectrum was collected in 43 segments, each of which is the Fourier transform of 250000 co-averaged FIDs. The analysis of adjacent spectra was performed using a Mathcad script. The total measurement time was approximately 90 h.

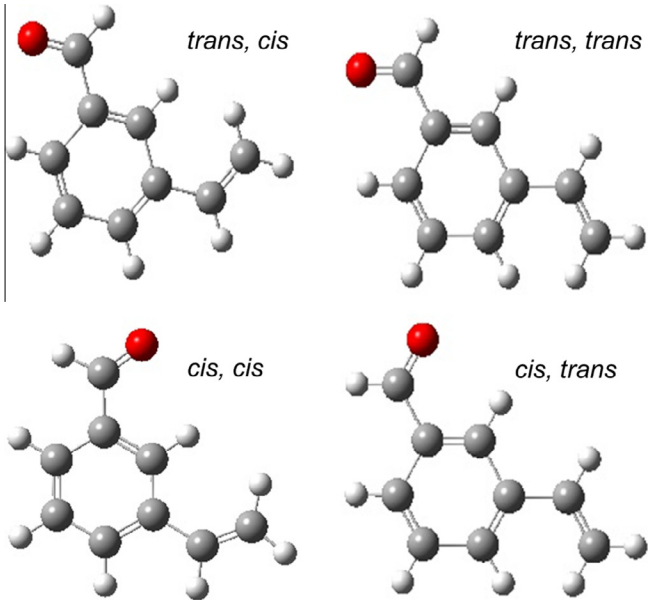

Fig. 1. Four stable conformers of 3VBA are shown with labels. The first label corresponds to the orientation of the oxygen atom with respect to the vinyl group, and the second label corresponds to the orientation of the C=C double-bond with respect to the aldehyde group. All four conformers are approximately planar.

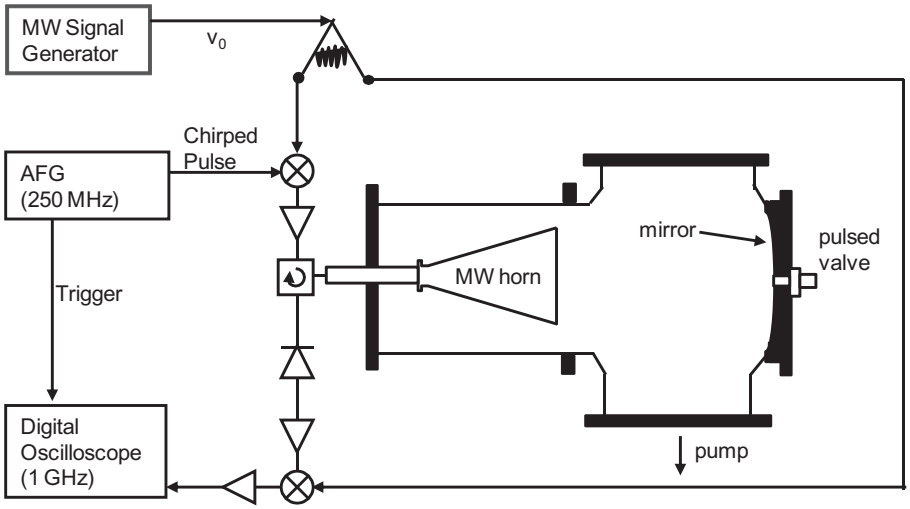

Fig. 2. A diagram of the chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer. The spectrometer uses chirped microwave pulses to measure the 8–18.5 GHz spectrum in 500 MHz segments. A single microwave horn antenna is used for both broadcasting the microwave polarizing pulse and collecting the molecular free induction decay. The molecular sample is introduced into the vacuum chamber by a pulsed valve through a small hole in the mirror, thus achieving a coaxial orientation between the pulsed valve and the microwave radiation.