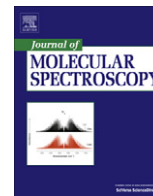




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Rapid capture of large amplitude motions in 2,6-difluorophenol: High-resolution fast-passage FT-MW technique

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ABSTRACT

The rotational supersonic-jet Fourier transform microwave (FT-MW) spectra of the aromatic 2,6-difluorophenol (DFP) have been recorded and analyzed in the frequency range of 8–26 GHz. A new design of broadband FT-MW spectroscopy with in-phase/quadrature-phase-modulation passage-acquired-coherence technique (IMPACT) has been used to obtain the spectra rapidly at high-resolution, obsoleting subsequent measurements with a resonator spectrometer.

The structural analysis shows that the H-atom of the hydroxyl-group is located in the benzene plane forming an intramolecular hydrogen bond with one of the F-atoms. Due to the tunneling motion of this H-atom between two the equivalent positions, a large part of the rotational transitions are split into two signals being separated by ~17 MHz.

The rotational constants, centrifugal distortion constants and the Coriolis coupling constant have been determined.

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1. Introduction

The present study on 2,6-difluorophenol follows our interest to examine molecules with large amplitude internal motions by the high resolution of microwave spectroscopic techniques. The combination of supersonic-jets with FT-MW spectroscopy [1,2] is a powerful tool in the investigation of large amplitude motions of gas phase molecular systems.

In this work, we have analyzed the rotational spectra of 2,6-difluorophenol using a new design of a linear fast passage (“chirp”) FT-MW spectrometer [3–5] called IMPACT: In-phase/quadrature-phase-Modulation Passage-Acquired-Coherence technique. This new approach provides instant broadband performance using fast linear frequency sweeps (chirps), instead of on/off-modulated CW radiation (pulses), to polarize the sample. Details of the design are given in the next section. Initial assignments of the observed emission lines were made with the aid of high level ab initio calculations. Being of interest due to formation of intramolecular hydrogen bonds, rotational spectra of mono- and dihalogenated phenol have been extensively studied [6–12]. Similar to other phenol derivatives the hydroxyl-group may internally rotate relative to the frame of the molecule (Fig. 1), with the two parts of the molecule found to be in-plane in their equilibrium configuration. This

motion can be considered as a tunneling process through a low barrier which inverts the μ_a dipole moment component.

Contrary to the study of 2,4-difluorophenol [13] which is asymmetrically substituted and thus adopts a single equilibrium structure, 2,6-difluorophenol exhibits two geometrically equivalent equilibrium configurations.

2. Experimental section

The spectra were obtained using the IMPACT-FT-MW spectrometer in Hannover and was constructed in parallel to a similar instrument located at the University of Valladolid [14]. Direct use of a commercial sample of 2,6-difluorophenol, without any further purification, was made. For the experiments described here, the sample – a solid at room temperature – was placed in a reservoir within the solenoid pulse valve and heated to 50 °C to seed 2,6-difluorophenol in the carrier gas, Ne or Ar. A backing pressure of 2 bar was used to achieve the supersonic jet-expansion.

A block diagram of the supersonic-jet expansion linear fast passage (FP) FT-MW spectrometer discussed here is presented in Fig. 2. With the general design considerations regarding its high-frequency electronics being instructive for FP-based methods in general [15,16] it provides some specific performance advantages. The design implements the IMPACT excitation process by using a single-stage in-phase/quadrature-phase (I/Q) modulation scheme for direct single-sideband frequency conversion. The IMPACT spectrometer (see Fig. 2) uses a short MW radiation frequency ramp for

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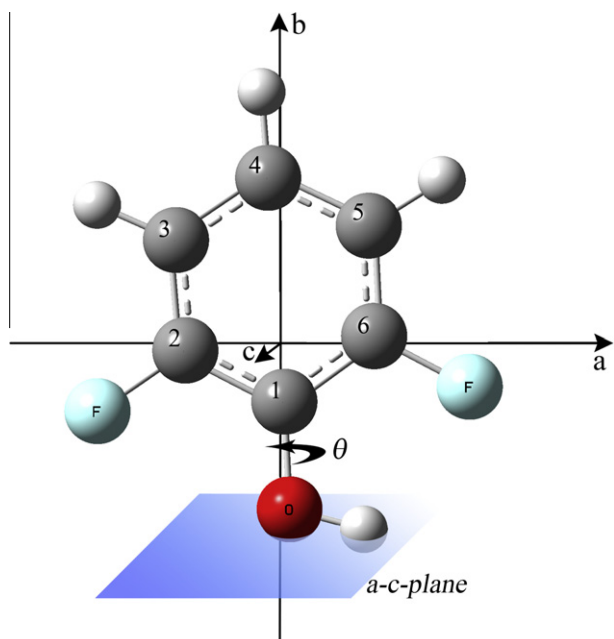


Fig. 1. 2,6-Difluorophenol with definition of the principal inertia axis system.

excitation and in this particular implementation uses components that allow for frequency coverage from 2 to 26.5 GHz. The principle of operation of this relatively simple set-up – compared to typical FT-MW instruments – is as follows: A primary signal with frequency ν is generated by the signal generator (1). Employing a pin-diode single-pole-double-throw (SPDT) switch (2a), this signal is either used for excitation or for detection. In the first case, a short MW frequency ramp centered at ν has to be created with sufficient

microwave power for the FP excitation of the molecules. In the second case, the microwave response of the probe has to be converted – taken as a difference frequency signal between the molecular and the primary radiation at frequency ν – into a lower-frequency band, the so-called base band. Similar to the coaxially oriented beam-resonator arrangement (COBRA) FT-MW apparatus, [17–19] the primary signal source is not used directly for the molecular excitation. The output signal of an single-sideband up-converter (5) is utilized instead. However, in contrast to the narrow-band (<1 MHz) excitation scheme of the COBRA apparatus, where the single-sideband modulator is used to generate a specific fixed frequency, in the IMPACT instrument a broad-band (<1 GHz) single-sideband frequency ramp $\nu + \Delta\nu(t)$ is created via I/Q modulation at frequencies $\Delta\nu(t)$ in the range $-500 \dots +500$ MHz, centered at DC, invoking an arbitrary-signal generator (3) and a matched pair of DC-coupled amplifiers (4). As a consequence of two RF signals swept from 500 MHz through DC and back to 500 MHz while alternating the quadrature phase sense, two low and high frequency half-bands are generated thus creating the broad-band frequency ramp centered at ν . This ramp, with its generation principle inherently warranting for invariant phase repeatability, is used for excitation. The power level necessary for the polarization of the molecular systems is adjusted via the amplitude of the modulation frequency; using a variable attenuator is optional. A 1 W solid-state high-power amplifier (6) is used in the presented instrument which employs a special horn/reflector antenna configuration to achieve strong polarization fields as described below. Compared to a conventional horn antenna setup the use of a high-power traveling-wave-tube (TWT) amplifier is not necessary for quite polar molecules like 2,6-difluorophenol. High power levels become necessary because of the spectral width of 1 GHz, which is swept in $\tau_p = 10 \mu\text{s}$ typically.

A pin-diode single-pole-single-throw (SPST) switch (2b) isolates the molecular interaction zone during the detection from noise of

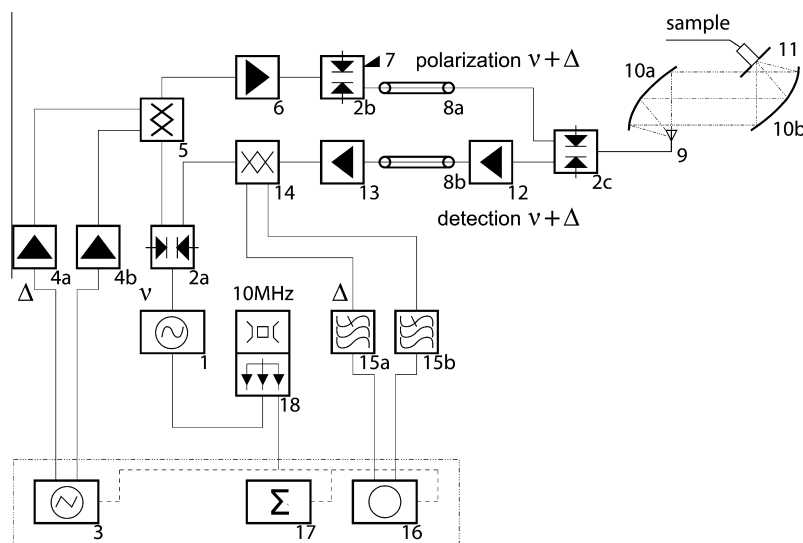


Fig. 2. Supersonic-jet expansion IMPACT Spectrometer: (1) MW signal generator, Agilent E8257D, 2–40 GHz, 9 dBm output power; (2) MW SPDT pin-diode switch, Sierra Microwave Technology SFD0526-001S, 0.5–26 GHz, 50 dB isolation, 3 dB insertion loss; (3) RF arbitrary-waveform generator, Agilent technologies N6030A, 2×1.25 Gs/s generation, 15 bit resolution; (4) RF DC-coupled amplifier, FAST TA2400, DC–2.4 GHz; (5) MW I/Q-upconverter, Miteq SM0226LC1MDQ, 2–26 GHz, 15 dB carrier suppression, 12 dB insertion loss; (6) MW 1 W high-power amplifier, Agilent 83020A, 2–26.5 GHz, 10 dB noise figure, 30 dB gain, 30 dBm output power; (7) Termination, Aeroflex TS260 M, DC–26 GHz; (8) MW flexible coaxial cable, United Microwave Products Microflex 150, DC–26.5 GHz; (9) MW dual-ridge horn antenna, Satimo SH2000, 2–32 GHz, 20 dBi gain; (10), parabolic reflector, Satimo reflector with interface for SH2000, 2–32 GHz; (11) Planar reflector with solenoid valves, General Valve series 9; (12) MW very-low-noise amplifier, Miteq JS4-02002600-28-5P, 2–26 GHz, 2.8 dB noise figure, 30 dB gain, 5 dBm output power; (13) MW low-noise amplifier, Miteq JS4-02002600-30-10P, 2–26 GHz, 3.0 dB noise figure, 30 dB gain, 10 dBm output power; (14) MW I/Q-downconverter, Miteq IRM0226LC1Q, 2–26 GHz, 18 dB image rejection, 14.5 dB insertion loss; (15) RF lowpass filter, Reactel 10L3-495-S11, DC–495 MHz, 2 dB insertion loss; (16) RF Digitizer, Agilent U1061A-002, 2×1 GS/s real-time acquisition; (17) PXI-chassis based experiment control, data-acquisition, and –analysis system, National Instruments e1065/6602/6221/e8106; (18) GPS-disciplined Rubidium Clock 10 MHz Frequency standard with distribution amplifier, Hewlett Packard 58533A, 5×10^{-11} frequency stability, Stanford Research FS725, 5×10^{-10} frequency stability; Hewlett Packard 58502A, 10×10 dBm output power.

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