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Internal rotation and structure of thiophenol and 4-fluorothiophenol studied by microwave spectroscopy and quantum chemistry

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ABSTRACT

Microwave spectra of two isotopologues of thiophenol, (C_6H_5–SH and C_6H_5–SD), and one of 4-fluorothiophenol (4-F–C_6H_5–SD) were investigated. As a consequence of the internal rotation the vibrational ground state consists of two torsional sub-states and the rotational transitions appear as doublets in the spectra. Rotational constants and centrifugal distortion constants for both sub-states and energy difference and a Coriolis type interaction parameter between the sub-states were determined. For thiophenol eleven parameters, including potential constants, structure parameters and parameters describing relaxation of structure during internal rotation, were adjusted to give an accurate global fit to microwave spectroscopic constants for the two isotopologues and far infrared data for the parent species. For 4-fluorothiophenol the microwave spectra were assigned for the SD-species only, good infrared data were not available, and only seven parameters could be determined. The barrier to internal rotation was determined to 277 cm^{-1} for thiophenol and 62.5 cm^{-1} for 4-fluorothiophenol. Both molecules were found to be planar in the equilibrium configuration. *Ab initio* calculations using B3LYP, MP2 and CCSD(T) were used not only to compare with the experimental parameters, but also in the choice of experimental parameters, in particular the relaxation parameters. Problems due to linear dependencies for larger basis sets are discussed.

1. Introduction

The microwave spectrum of thiophenol was first reported by Johansson et al. 1967 [1] Only μ_a lines were assigned and no splitting due to internal rotation was reported. The molecule was found to have a small inertial defect and was therefore assumed to be planar.

The MW-spectra used in the present study were recorded by us in 1973 and some results for the parent species of thiophenol were published together with IR-data. The molecule was found to be planar in the equilibrium configuration and the height of the barrier to internal rotation was found to 267 cm^{-1} [2].

After many years where the planarity of thiophenol could not be confirmed by *ab initio* calculations, Remacle et al. in 2004 using DFT-calculations found a planar equilibrium structure and barrier heights in the range from 69 to 474 cm^{-1} [3].

From spectroscopic studies the barrier in 4-fluorophenol is known to be smaller than that of phenol, 1006 cm^{-1} [4] versus 1213 cm^{-1} [2], and it seems worthwhile to investigate whether a similar effect can be found in 4-fluorothiophenol compared to thiophenol.

The general features of the rotational torsional energy levels and microwave spectra are similar to those of phenol and 4-halogenophenols. Due to internal rotation, the vibrational ground state is split into two torsional sublevels separated by the torsional or tunnelling splitting. The lower of the two sub-states is called '+' and the upper '–' according to the symmetry of the state with respect to the permutation in the molecular symmetry group [5]. On top of each of the torsional states there is a complete rotational energy level system described by rotational constants and centrifugal distortion constants. This relatively simple picture is disturbed by one or more couplings of Coriolis type between the two sub-states [4]. The rotational spectrum consists of μ_a- and μ_b-transitions which are all seen in the spectrum as doublets. The torsional sublevel is not changed during μ_a-transitions, meaning that these transitions consist of one rotational line for the '+' state and one for the '–' state. The doublet splitting is relatively small for μ_a-transitions because it is mainly determined by the differences between rotational constants for the two sub-states. On the other hand μ_b-transitions going from one torsional sublevel to the other, have a much larger splitting which is to a first approximation equal to twice the torsional splitting.

In the present study microwave spectroscopic results for two isotopologues of thiophenol were combined with far infrared results in a single fit to molecular parameters. In this way it became possible to determine not only the internal rotation potential

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function but also some structural parameters for the molecule as well as relaxation parameters describing how the structure changes during the internal rotation. In the case of 4-fluorothiophenol for which the barrier turns out to be much lower and the effect of the internal rotation, in particular the splitting of the rotational transitions, therefore much larger than in thiophenol, the MW-spectra were only assigned for the deuterated species (FC_6H_5SD), and a smaller number of parameters were determined.

Because we wanted to compare *ab initio* calculations with accurate experimental potential constants, structural parameters and changes in structure during the internal rotation, and because we wanted to use the *ab initio* calculations as a guideline in the choice of relaxation parameters, it was decided to use not only DFT-calculation but also MP2 and CCSD(T) calculations.

2. Experimental

The microwave spectra were recorded on conventional Stark modulated MW-spectrometers (E40-8400B and HP8460A) covering the spectral region 8–40 GHz. The spectra were measured at 1–2 Pa, −30 °C for thiophenol and at 3–6 Pa, −20 °C for 4-fluorothiophenol. Radiofrequency microwave double resonance was used in the assignment of some lines in 4-fluorothiophenol-SD by replacing the Stark modulation by a square wave amplitude modulated radiofrequency signal between 5 and 120 MHz [6].

The parent compounds were commercially available and the deuterated species were prepared by exchange with deuterated methanol.

Microwave spectra were not assigned for the parent species of 4-fluorothiophenol. However, far infrared spectra of this molecule were recorded between 20 and 200 cm^{-1} on an interferometer (RIIC, type FS-520, see Ref. [2]) at 31 °C and at the vapor pressure of the compound. The spectra were disturbed by interference patterns in the region below 50 cm^{-1} where the fundamental frequency of the torsional mode was expected, and the far infrared spectra were therefore not used in the determination of spectroscopic constants. However, at higher frequency some broad bands could be attributed to transitions in the free rotor limit of the torsional mode.

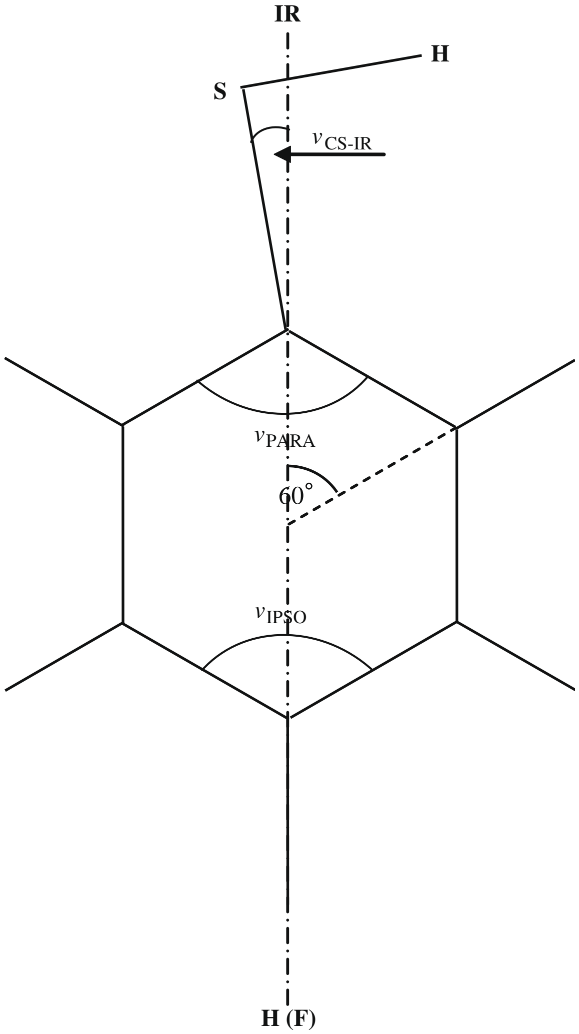

Fig. 1. Definition of some structural parameters.

3. Theory and methods

The rotation internal rotation calculations were based on a general model (SEMIRIG) which has the internal rotation of one part of the molecule (the top) against the other part (the frame) as the only internal degree of freedom and which has no symmetry restrictions on the two parts of the molecule [7]. This model was extended by allowing the molecular structure to depend on the internal rotation angle and was implemented in a program called SEMIRIG-RELAX.

In the case of thiophenol and 4-fluorothiophenol the SH-group was considered as the top and the phenyl ring as the frame. The planar configuration of the molecule was chosen as reference and was defined by the following assumptions and adjustable parameters (see Fig. 1): four parameters were used to define the structure of the top: two bond lengths, r_{CS} and r_{SH}, the bond angle v_{CSH} and the angle $v_{CS\text{-}IR}$ between the CS bond and the internal rotation axis which by definition passes through the carbon atoms 1 and 4 in the phenyl ring. The phenyl ring was assumed to have C_{2v} symmetry with the C_2-axis coinciding with the internal rotation axis; the angle between the C_2-axis and any of the ortho and meta CH-bonds was assumed to be 60°. Assuming finally all CC bond lengths to be equal and the same for all CH bond lengths, the structure of the ring could be described using four parameters: one common CC distance, r_{CC}, one common CH distance, r_{CH}, and two CCC angles, v_{IPSO} and v_{PARA}. In the case of 4-fluorothiophenol the CF-distance had to be included as an extra parameter.

Several different parameters for structure relaxation were considered, but finally it was decided to let the four internal coordinates for the top depend on the internal rotation angle γ in the following way:

$$q(\gamma) = q(0) + \frac{R(q)}{2}(1 - \cos(2\gamma)) \tag{1}$$

q is here the internal coordinate in question, and $R(q)$ the corresponding relaxation parameter for q. It is seen that $R(q)$ is the value of q in the perpendicular configuration ($\gamma = 90°$) minus the value of q in the planar configuration ($\gamma = 0°$). The phenyl ring plane was kept planar during the internal rotation.

For thiophenol the parameters for the internal rotation potential function are the constants V_2, V_4 in a Fourier expansion of the form

$$V(\gamma) = \frac{1}{2}\sum_{n=1} V_{2n}(1 - \cos(2n\gamma)) \tag{2}$$

In trying to fit the molecular parameters to the observed spectra some problems are encountered.

The first one is that although the SEMIRIG-RELAX program can be used to calculate rotational torsional transitions for low J values, it not suitable for high J values because the number of basis func-