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Vibrational spectroscopic study of 2-fluorophenol and 2,3,5,6-tetrafluorohydroquinone

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Abstract

The vibrational properties of two fluorophenol derivatives, 2-fluorophenol (**1**) and 2,3,5,6-tetrafluorohydroquinone (**2**), have been studied by FT-IR and FT-Raman spectroscopy. The spectra revealed the existence of two conformers for both compounds. A quantum chemical study of the title compounds was carried out at the B3LYP/6-311++G** level of theory. The computed harmonic force fields were scaled utilizing previously developed scale factors resulting in good agreement with experiment and facilitating the assignment of the vibrational spectra and a distinction between the two conformers. The wavenumbers of identified OH torsional modes support a stronger intramolecular O–H···F hydrogen bonding in **1** than in **2**.

Keywords: FT-IR; FT-Raman; Scaled quantum mechanical method; DFT computations; Conformation

1. Introduction

According to the observations in inorganic salts, the fluoride anion belongs to the strongest hydrogen bond acceptors [1–3]. In contrast, studies of organic compounds containing C–F···H–X (X = O, N) inter- or intramolecular interactions pointed out that the F···H hydrogen bond in such systems is generally weak [4–12], even when analogous situations with oxygen acceptor show strong interactions [4,7]. This is well represented by 2-fluorophenol possessing a weak intramolecular C–F···H–O hydrogen bond [6,12–19] in contrast to the strong C=O···H–O interaction in related oxo-derivatives (see e.g. [20]).

Recently we have performed a systematic computational study of 2-fluorophenol (**1**), 2,3,5,6-tetrafluorohydroquinone (**2**) and 2,6-difluorophenol (**3**) [6]. Using the MP2/6-31+G**//MP2/6-31G** level of theory, we elucidated the characteristic energetic and structural properties of these intramolecular hydrogen-bonded systems. The computations revealed a slight shortening of the hydrogen bond distances in the order $\mathbf{1} > \mathbf{3} > \mathbf{2}(C_{2h}) > \mathbf{2}(C_{2v})$. This trend was not clear from the gas electron diffraction experiments [11,12] due to the small differences hidden by the experimental errors. Parallel with the studies on the molecular geometry we also started a comparative spectroscopic investigation of the three compounds. We have published the FT-IR and FT-Raman spectra and the normal coordinate analysis of **3** [21].

In the present study we report the FT-IR and FT-Raman spectra of 2-fluorophenol (**1**) and 2,3,5,6-tetrafluorohydroquinone (**2**) and the normal coordinate analysis

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of the two compounds. We focus here on the vibrational characteristics of the intramolecular hydrogen bonding interaction. Vibrational spectroscopy has proven to be very effective in the study of hydrogen-bonded systems facilitating also the analysis of equilibria of the hydrogen-bonded and non-hydrogen-bonded conformers (appearing often in the case of weak intramolecular interactions). Among the vibrations most informative are the stretching and torsional modes of the donor XH (X = O, N, halogen) group. The weakening of the XH bond upon hydrogen bonding is accompanied by a decrease of the XH stretching wavenumber, while the hindered XH torsional motion results in a characteristic high-wavenumber shift (blue-shift) of the torsional mode.

The vibrational spectra of the present two fluorophenol derivatives (**1**, **2**) may characterize the small differences between the hydrogen bonds of the three derivatives. The vibrational spectra often consist of close-lying absorption bands of the two conformers, and in order to aid their interpretation, we have introduced the matrix-isolation technique in the present analysis.

2. Experimental

Commercial samples of 2-fluorophenol and 2,3,5,6-tetrafluorohydroquinone (Aldrich 98%) were used after checking their purity by gas chromatography. The solid, liquid and high-temperature gas-phase FT-IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer using an MCT detector and KBr windows in the mid-IR range (4000–450 cm^{-1}), whereas a DTGS detector and polyethylene windows were employed in the far-IR range (650–150 cm^{-1}). The solid and solution samples were measured at a spectral resolution of 4 cm^{-1}, accumulating 16 scans. The solutions were diluted until a concentration of ca. 0.1 M, when the intermolecular hydrogen bonding interactions between the solute molecules vanished. In the high-temperature gas-phase experiments on **1**, a temperature controlled 10 cm gas cell (Graseby Specac) and the following experimental conditions were used: $T = 323$ K, ~10 torr vapour pressure, 0.5 cm^{-1} resolution and 128 scans.

The room temperature gas-phase spectra were obtained in the range of 4000–450 cm^{-1} using a Bruker IFS88 spectrometer equipped with an MCT detector and interfaced to a 250 L electropolished stainless steel smog chamber equipped with a White-type multiple reflection mirror system with a 120-m optical path length for rovibrationally resolved infrared spectroscopy. The spectra were recorded with a resolution of 0.5 cm^{-1} using 100 scans.

Matrix-isolation IR spectra were recorded with a Bruker IFS66 FT-IR spectrometer at 0.5 cm^{-1} resolution. The samples were diluted with argon and alternatively with nitrogen (1:1000) and the mixtures were deposited on a CsI window at 5 K in a Displex model HS-4 cryostat (from APD) equipped with a three-stage cooling system. The spectra of the unannealed matrices were first recorded and subsequently annealed to 15 and 20 K to observe reorientations in the matrices. Further annealing to 25 and 30 K were carried out and the matrices were re-cooled to 5 K before recording the spectra.

The Raman spectra were measured in the range of 4000–150 cm^{-1} with a Nicolet Model 950 FT-Raman spectrometer at 2 cm^{-1} resolution using the 1064 nm line of a Nd:YAG laser for excitation (at 100–600 mW output power) and 180° scattering geometry. In general, 512 scans were co-added. Depolarisation measurements were performed on the liquid of **1** with the same setup using a built-in polarisation analyser set parallel and perpendicular to the electric vector of the exciting laser beam. The solvent spectra were subtracted from those of the solution measured under the same conditions. The Raman spectra communicated here are not corrected for instrument response.

3. Computational details

Quantum chemical DFT computations were carried out using the GAUSSIAN03 suite of programs [22] employing the Becke3–Lee–Yang–Parr (B3LYP) functional [23,24] in conjunction with the 6-311++G** basis sets. The Cartesian representation of the theoretical force constants were computed at the fully optimised geometry.

Natural internal coordinates were automatically generated by the program INTC [25]. The Cartesian force field was transformed to internal space using the program TRA3 [26]. Calculation of the scaled wavenumbers was done with the program SCALE3 [27,28]. Pulay's standard scaling method [29] was used, in which the theoretical (unscaled) force constant matrix F is subjected to the congruent transformation $F' = T^{1/2}FT^{1/2}$, where F' is the scaled force constant matrix and T is the diagonal matrix, containing the scale factors t_i. We used the scale factors developed recently for the B3LYP/6-311++G** force field of 3-trifluoromethylphenol [30], given as Supplementary Material of the present paper. As these scale factors performed very well for both **1** and **2**, we omitted any adjustment to the experimental data in the present study. The quality of the obtained data is assessed by the root-mean-square deviation between the experimental and scaled wavenumbers. For characterisation of the normal modes, their total energy distribution (TED) [31,32] among the various kinds of internal coordinates is used.

4. Results and discussion

4.1. Computed structures and hydrogen bonding

The conformations of **1** and **2** have recently been investigated at the MP2/6-31+G**//MP2/6-31 G** level [6]. In order to assess the performance of our B3LYP/6-311++G** method, we compare in Table 1 a few selected bond distances with previous data obtained by MP2 computations [6] as well as from gas-phase IR [18] and electron diffraction [11,12] experiments. The computed structures