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Hydrogen bond docking preference in furans: O—H···π vs. O—H···O

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ABSTRACT

The docking sites of hydrogen bonds in complexes formed between 2,2,2-trifluoroethanol (TFE), furan (Fu), and 2-methyl furan (MF) have been investigated. Using density functional theory (DFT) calculations, gas phase and matrix isolation FTIR spectroscopies, the strengths of O—H···O and O—H···π hydrogen bonds in the complexes were compared to find the docking preference. Calculations suggest that the hydrogen bond donor, TFE, is more likely to dock onto the oxygen atom of the aromatic furans ring, and consequently, the O—H···O type hydrogen bond is relatively stronger than the O—H···π type. The FTIR spectrum in the OH-stretching fundamental range obtained at room temperatures has been compared with that obtained at extremely low temperatures in the matrix. The fundamental and the red shifts of OH-stretching vibrations were observed in both FTIR spectra, confirming the formation of hydrogen bonded complexes. By assessing the ability of furan and MF to participate in the formation of O—H···O hydrogen bond, the effect of ring methylation has been highlighted. From the calculated geometric and thermodynamic parameters as well as the frequency shift of the OH-stretching vibrations in complexes, TFE–MF is found to be more stable than TFE–Fu, which suggests that the strength of the O—H···O hydrogen bond in TFE–MF originates from the high activity of the furan molecule caused by the methylation of the aromatic ring. The present study furthers the knowledge of docking preference in heteroaromatic molecules and is helpful to understand the nature of intermolecular interactions between hydrogen bond donors and acceptors, including both electron-deficient atoms and π cloud.

1. Introduction

Heteroaromatic compounds constitute a considerable fraction of the total volatile organic compounds (VOCs) in urban atmosphere, which is well known to be an important component in the atmosphere affecting climate forcing and carbon cycling [1–5]. Additionally, the heteroaromatic organic content is dominantly responsible for the secondary organic aerosol (SOA) formation. The atmospheric oxidation of aromatic hydrocarbons in the atmosphere forms various non-volatile and semi-volatile organic compounds, which play essential roles in the formation of urban SOAs [6–8]. Hence, the atmospheric chemistry of aromatics is vitally important for understanding the formation of urban SOAs. Among all the aromatic hydrocarbons, heterocyclic organic compounds containing oxygen, such as, furan and some of its derivatives are an important group of atmospheric pollutants. They are both primary and secondary pollutants in the atmosphere, and their emission contributes to the formation of ultrafine particles and ground-level ozone [9,10]. Besides, furans can react with atmospheric radicals and affect the oxidative budget of the lower troposphere [11]. The atmospheric source of furan includes emissions from agricultural processes, atmospheric oxidation reactions of 1,3-butadiene and 1,3-pentadiene, tropical forest burning, food processing and direct emissions from plant material [1,12,13]. In order to evaluate the atmospheric behavior of heteroaromatic furans, it is important to study their interaction with other atmospheric molecules.

Although aerosol particles greatly affect climate by scattering sunlight, their formation mechanisms in the atmosphere at detailed molecular level and the exact participating molecules still remain largely unknown, despite recent advances in the field of aerosol science [14–18]. For instance, Almeida et al. have found that both amines and sulfur dioxide can enhance new particle formation in regions of the atmosphere near amine sources [14]. Besides well-known species such as sulfuric acid, ammonia, amines, and various organics participating in this process, alcohols like methanol, ethanol and 2,2,2-trifluoroethanol (TFE) are also capable of forming intermolecular hydrogen bonded complexes through the hydrogen atom of their hydroxyl groups and an electronegative atom of a second molecule. All these three kind of alcohols are widely used in experiments as possibly candidate species for the atmospheric complexes study, and TFE is shown to be the strongest hydrogen bond donor among these three kinds of alcohols to drive gas to particle conversion [19–22]. While some furan molecules have been shown to be good hydrogen bond acceptors [23], their bindings with TFE are weakly explored. In the present study, TFE is chosen as the OH donor molecule for the formation of selected furans complexes. The hydrogen bonded interactions between TFE and heteroaromatic furans may provide the possibility for the formation of atmospheric aerosols,

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and a better assessment of the atmospheric behavior of some heterocyclic compounds.

Infrared (IR) spectroscopy has been proved to be an ideal technique for the detection of hydrogen bonds, from which frequency shifts and changes in the band intensities can be obtained [24–27]. A variety of experimental techniques have been used to help determine the properties of hydrogen bonded complexes, including matrix isolation FTIR [28–30], gas phase FTIR [31–33] and supersonic jet FTIR [34–36]. Owing to low temperatures, the matrix isolation FTIR spectroscopy is considered as a useful analytical technique for observing and characterizing hydrogen bonded interactions in complexes [28–30]. As a result, a series of experiments have been carried out to study the intermolecular interactions between sulfuric acid and several molecules of atmospheric interest using matrix isolation spectroscopic methods. Several new bands observed from the matrix isolation FTIR spectra indicated the existence of the 1:1:1 $H_2SO_4/CH_3OH/H_2O$ cyclic complex [37]. Gas phase FTIR is the simplest and most convenient method in the investigations of hydrogen bonded complexes [31–33]. The experimental temperature of gas phase FTIR remains within few degrees of ambient temperature, being much higher than the temperature in the jet expansion cooling and matrix isolation processes. For instance, intending to determine the minimum energy structure and interaction energy of dimethylamine (DMA)—trimethylamine (TMA) hydrogen bonded complexes by gas phase FTIR, the experimental temperature was 298 K [32]. Gas phase FTIR spectra of 1:1 complexes of MeOH with DMA and TMA were measured in the temperature range 298 K–358 K, and the results suggested that the enthalpy becomes more negative with increasing temperature [33]. The supersonic jet FTIR techniques are suitable for diagnostics of supersonic expansions involving cluster formation, especially for small clusters and larger aggregates [38].

The competition between π and oxygen binding has caused much attention in recent years. The detection of the hydrogen bond docking preference for different classes of aromatic compounds represented by furan (Fu), benzofuran and 2,5-dimethyl furan has been performed [39–42]. In a previous work, we explored, for the first time, the docking site of hydrogen bonded MeOH–furan complexes using matrix isolation FTIR spectroscopy [23]. According to the optimized geometries by theoretical computation, we found that the hydrogen bond ability of furan is not just restricted to the lone pair of the oxygen. Instead, the hydrogen bond donor molecule may also interact with the π system of the furan ring. To describe the strength and docking preference of these two kinds of hydrogen bonds, the geometric and thermodynamic parameters along with the calculated and observed red shifts of the OH-stretching fundamental transitions of MeOH were compared, and the results showed that stabilizing interactions formed by O—H···O hydrogen bond are more accessible. Although carried out by different experimental conditions, all the related investigation confirms the formation of weak intermolecular hydrogen bond to a π cloud. In addition, the reactivity of aromatic molecules can be adjusted systematically by ring substitution due to their delocalized π cloud. A recent investigation of the methylation of aromatic anisole to change the π cloud attractivity has been undertaken by supersonic jet FTIR [34]. The spectroscopic method of determining the docking preference of MeOH to anisole revealed that the subtle balance between these two structures can be varied by one order of magnitude through single to triple methylation of the aromatic ring and introduction of a single *tert*-butyl substituent.

In the present work, we study the effect of the aromatic ring methylation on the stability of the hydrogen bonded complexes. The hydrogen bonds between TFE and heteroaromatic furan, and 2-methylfuran (MF) were investigated using gas phase and matrix isolation FTIR spectroscopy. Quantum chemical calculations on the TFE–Fu and TFE–MF complexes were performed to help determine the most stable conformers and interpret the spectra. Here, we focus on considerably weaker hydrogen bonds in TFE–furans complexes involving oxygen acceptor sites. The goal is thus to establish experimental docking preferences for TFE to heteroaromatic compounds. We investigate how the ring methylation affects the hydrogen bond structures. Atoms in molecules (AIM) analysis has also been performed to understand the nature of interactions in the furans complexes.

2. Experimental and Computational Methods

2.1. Experimental Details

TFE (99.9%, Aladdin), furan (99%, Aladdin) and MF (99%, Aladdin) were purified with multiple freeze-pump-thaw cycles on a vacuum line before use. The room temperature gas-phase IR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer using 1 cm^{-1} resolution and 128 scans. A KBr beam splitter and a DLaTGS detector were fitted to the spectrometer. A 20 cm path length gas cell equipped with CaF_2 windows was used to measure the spectra. The mixtures were prepared in the gas cell, which was connected to a vacuum line with a base pressure of less than 1×10^{-4} Torr. The pressure was measured with Tamagawa CDG-800 pressure gauges connected to the vacuum line. The details of the experiments have been described elsewhere [19].

The matrix isolation spectra were recorded with our matrix isolation apparatus, using a closed-cycle helium compressor cooled cryostat (PT-SHI-4-5, Janis Research Company, USA) to achieve low temperatures. The cryostat was housed in a vacuum chamber. A pressure gauge (WRG-NW25, Edward, UK) was used to monitor the pressure inside the cryostat chamber. The base pressure of 10^{-5} mbar was generally recorded at the beginning of an experiment. Regulated by a temperature controller (model 22C, Cryocon, USA), temperatures at the cold surface were measured with a silicon diode sensor (DT-670, Lakeshore, USA). The substrate was put in the sample beam of a FTIR spectrometer to allow spectral measurement. Argon (99.999%, Deyang special gas company) was used as the matrix gas. TFE, furan and MF were used without further purification. The argon/sample ratio was 1/700. The infrared spectra of the deposited samples were recorded at 0.5 cm^{-1} resolution with a Vertex 80v FTIR spectrometer (Bruker) fitted with a KBr beam splitter and liquid nitrogen cooled MCT detector. The precursors were then separately deposited onto the diamond cold window at 14 K, the deposition was annealed to 25 K, 30 K, and 35 K, and maintained at each temperature for 30 min, and then re-cooled to 14 K. Spectra were recorded after each warming cycle to monitor any changes caused by these processes. All spectral subtraction and analysis were performed with OPUS 7.2 and Origin 9.0 software.

2.2. Computational Details

Gaussian 09 computational program package was used to perform all the calculations [43]. The geometries of monomers (TFE, furan, MF) and the complexes (TFE–Fu and TFE–MF) were optimized with the B3LYP, B3LYP-D3, M06-2X, and ωB97X-D functionals, using the aug-cc-pVTZ basis set on all atoms. All calculations were carried out using the "opt = verytight" and "int = ultrafine" options, which have shown to improve the calculations in giving good frequencies and thermochemical corrections to the electronic energies for the hydrogen bonded complexes [32]. The B3LYP-D3 functional, known to be superior to the conventional B3LYP functional by the inclusion of the D3 dispersion correction, significantly improves the description of noncovalent interactions [44]. This functional has been shown to provide appropriate results in characterizing atmospheric hydrogen bonded complexes [45]. Consequently, the results presented here are based on B3LYP-D3, while those from the M06-2X, ωB97X-D, and B3LYP are shown in the supplementary material. Geometries optimizations and harmonic vibrational frequency calculations performed on all the structures of the relevant monomers and complexes exhibited no imaginary frequencies, indicating that the calculated structures were minima on the potential energy surface. Thermal contributions to the energies were calculated under the harmonic oscillator-rigid rotor approximation [25]. Zero point vibrational energy (ZPVE) corrections for binding energies (*BE*) were obtained from unscaled DFT