

Infrared Spectroscopic Investigation on Solvent-induced Acidic CH Bonds Switching in Cationic Dimers of Cyclic Ethers

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[Introduction] Proton-transfer reaction is one of the most fundamental processes in chemistry and biology. Most of the proton-transfer reactions occur from a protic bond such as NH, OH, and SH. On the other hand, CH bonds are generally regarded as aprotic and generally ignored as a proton donor. However, many examples of product ions which originate from proton transfer from CH have been observed in mass spectrometry.

Very recently, we have demonstrated proton-transfer occurs from a CH bond in the photoionized dimer of tetrahydrofuran (THF). Furthermore, enhancement of the acidity of the CH bonds in a bare THF cation has been shown by the spectral signature of the CH stretch vibrations. These results indicate that the CH bonds of cationic THF are highly acidic. This enhancement of the acidity is explained by the hyperconjugation between the singly occupied molecular orbital (SOMO) of the O atom and the σ orbitals of the CH bonds.

Because tetrahydropyran (THP) is a six-membered ring molecule, it can form the chair and boat type conformers, which are geometrically hindered in the five-membered ring THF. One can expect that this structural difference would influence the magnitude of the interaction (hyperconjugation) between SOMO and CH bonds. Therefore, the correlation of the acidity of cationic CH and the conformation can be investigated by comparing the THP and THF cations.

In this study, we carried out the IR spectroscopy of the THP monomer and dimer cations, which are generated through the VUV photoionization. The theoretical calculations for geometries, vibrational spectra, proton-transfer potential energy curves, and electron spin density distribution have also been performed. The acidity of cationic CH and the proton-transfer reaction from CH in ionized THP are discussed through comparison of IR spectroscopic and theoretical results.

[Experiment and Calculations] The IR spectra of the THP monomer and dimer cations were observed by the IR predissociation spectroscopy of VUV-pumped cation (IRPDS-VU-PI).[1] In this spectroscopy, size-selective IR predissociation spectra of cations, which are generated by the VUV photoionization at 118 nm, are recorded.

The isomerization reaction of the ionized THP dimer was simulated by the global reaction route mapping (GRRM) program [2] mounted on the Gaussian09 (G09) program. The structures, energies, and vibrational spectra were calculated with G09. The electron spin density distribution calculations of the cationic monomer and the dimers along the isomerization process also have been performed.

[Results and Discussion] Figure 1 shows (a) the observed IR spectra of the cationic THP monomer and the calculated spectra for the (b) chair and (c) twist type structures inserted in the figure. Only these two structures are stable in the THP cation. In the observed spectrum, an intense band is seen at 2855 cm^{-1} . By comparing the observed and calculated spectra, we

assigned the spectral carrier of the observed one to the chair type structure which is the most stable structure. The observed intense band is assigned to the stretch vibration of the CH bond at the 4th position, indicated by the broken circle. The acidity of the CH bond is enhanced, because of delocalization of the σ bonding electron of C(4)H to the CC bonds and SOMO of the oxygen atom through the hyperconjugation.

Figure 2 presents (a) the observed IR spectrum of the THP dimer cation and (b)-(d) the simulated spectra of its three most stable structures. In the observed spectrum (a), the CH stretch bands are seen in the range of 2800~3000 cm^{-1} and a broad feature appears from 3100 cm^{-1} to the lower frequency region. The latter band is explained by the stretching vibration of the shared proton in the two most stable structures of the O...HO and C...HO types. Both of the structures are formed through the intermolecular proton transfer from the CH next to the oxygen of the ionized moiety. This CH acting as the proton donor is different from the acidic CH in the THP monomer cation. This result implies the acidic site is switched in the proton transfer process of the THP dimer cation from that of the bare cation.

We also carried out the intrinsic reaction coordinate (IRC) and GRRM reaction path search calculations, and the electron spin density distribution analysis. We will discuss the acidity enhancement of CH and the reaction mechanism of the proton transfer from CH based on the experimental and theoretical results.

[Reference]

- [1] Matsuda et al., *Phys. Chem. Chem. Phys.*, **2009**, 11, 1279-1290.
 [2] Ohno and Maeda, *Chem. Phys. Lett.*, **2004**, 384, 277-282.

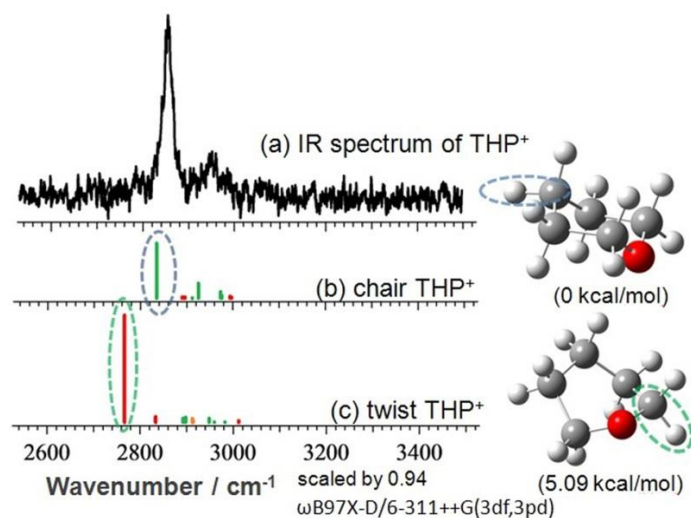


Figure 2. (a) The observed IR spectra of cationic THP and (b, c) its two optimized structures.

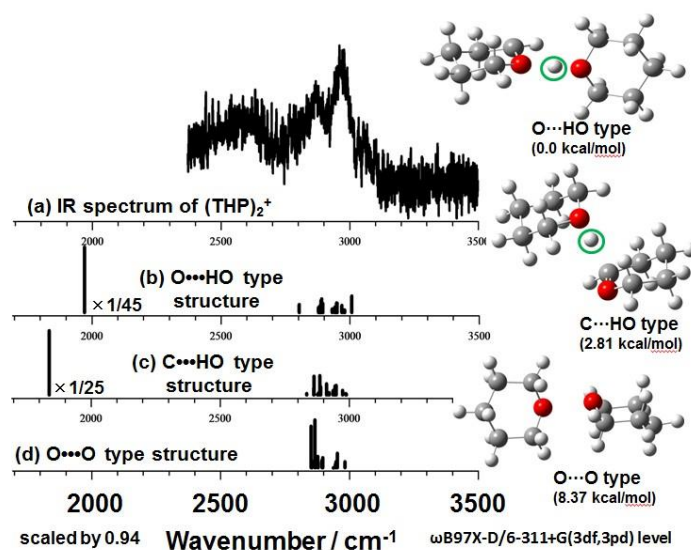


Figure 1. (a) The observed IR spectra of THP dimer cation and (b)-(d) its three optimized structures.