

## Proton-transfer from CH Bonds of Ionized Tetrahydrofuran (THF) Clusters

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**[Introduction]** Proton-transfer, which is one of the most fundamental reactions, has been concerned intensively, because of its key role in a variety of biological and chemical processes. It has been well-known that proton-donor abilities of cationic OH and NH bonds are higher than those of neutrals. Upon the ionization of clusters of protic molecules such as methanol, ammonia, and carboxylic acids, the barrier-less proton-transfer reactions have been identified from OH and NH bonds.[1] These results demonstrate strong acidities of cationic OH and NH.

Neutral CH bonds are ordinarily regarded as aprotic because of their low acidities. However, likewise cationic OH and NH, high acidities of CH may be expected in the cationic state. Tetrahydrofuran (THF) is composed only of the alkyl group and the oxygen atom which can act as a proton acceptor. Therefore, THF is a simple system to examine the proton donating ability of CH and the possibility of proton-transfer from CH.

In this study, we have performed infrared (IR) spectroscopy of the THF monomer and dimer cations, which are generated through the vacuum-ultraviolet (VUV) photoionization. Theoretical calculations of geometry optimization, vibrational spectra, proton-transfer potential energy curves, and natural bond orbital (NBO) analysis also have been performed for them. The acidity of CH of cationic THF is discussed through comparison of these IR spectroscopic and theoretical results.

**[Experiments and Calculations]** The IR spectra of the THF monomer and dimer cations were observed by IR predissociation spectroscopy of VUV-pumped ions (IRPDS-VUV-PI).[1] In this spectroscopy, size-selective IR predissociation spectra of cations, which were generated with the VUV photoionization at 118 nm, are recorded by monitoring the size-selected ion signal intensity of the parent ion under investigation or the fragment ion by use of the time-of-flight mass spectrometer.

The isomerization reaction of the ionized THF 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 simulated IR spectra were calculated at the UPBE1PBE/6-31+G(d) level with the scaling factor of 0.94.

**[Results and Discussion]** Fig. 1 shows (a) the IR spectrum of the cationic THF monomer obtained by monitoring the dehydrogenated THF cation channel, and (b) the calculated IR spectrum of the THF cation. In the observed spectrum, the intense CH stretch band is seen at  $2700\text{ cm}^{-1}$ , which is out of the normal CH stretch frequency range. This band is assigned to the symmetric stretch vibration of the CH bonds next to the oxygen atom. The extraordinarily low frequency of the band is due to the weakening of the CH bonds by the delocalization of the  $\sigma$  bonding electrons of CHs. This delocalization is caused by the hyperconjugation between the  $\sigma$

orbital and the singly occupied molecular orbital (SOMO) of the O atom. The hyperconjugation increases the acidities of the CH bonds.

Fig. 2 presents (a) the observed IR spectrum of THF dimer cation and (b, c) the simulated spectra of the stable structures of the THF dimer cations. In the observed spectrum, the broad and intense feature appears from 2900  $\text{cm}^{-1}$  to the lower frequency region. This broad feature is assigned to the H-bonded OH stretch. Among isomers of the THF dimer cation, two types of the most stable structures have H-bonded OH, as depicted in Fig. 2(b, c). One is the C $\cdots$ HO type, in which the C and O atoms intermolecularly share the proton, and the other is the O $\cdots$ HO type, in which the proton is located between the two O atoms. The spectral carrier of the observed spectrum is assigned to them because the broad and intense band is assigned to the H-bonded OH of these structures. Both of the structures are formed through the intermolecular proton-transfer from a CH bond of the ionized THF. This result demonstrates that the proton-transfer from CH occurs in the ionization of the THF dimer. Thus, both the results of the THF monomer and dimer cations indicate CH of THF cation is highly acidic.

We have also performed the intrinsic reaction coordinate (IRC) calculation for the proton-transfer potential curve and the GRRM reaction path search for the isomerization of the ionized THF dimer. We will discuss the acidity of THF cation and the isomerization of the dimer cation with these experimental and theoretical results.

## [Reference]

- [1] Y. Matsuda, *Phys. Chem. Chem. Phys.*, **2009**, 11, 1279-1290.  
 [2] K. Ohno, S. Maeda, *Chem. Phys. Lett.*, **2004**, 384, 277-282.

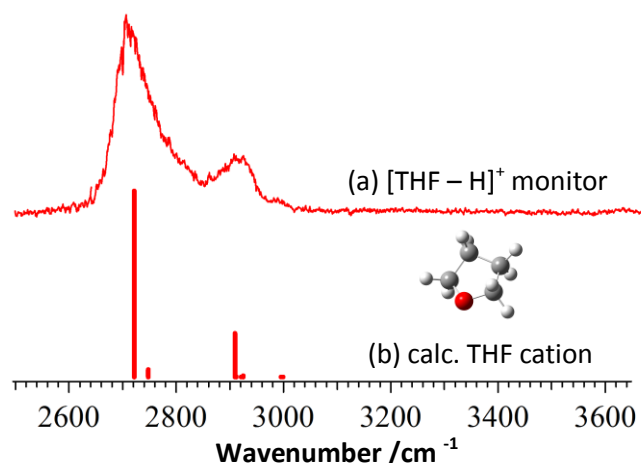


Figure 1. (a) Observed and (b) calculated IR spectra of cationic THF and its optimized structure.

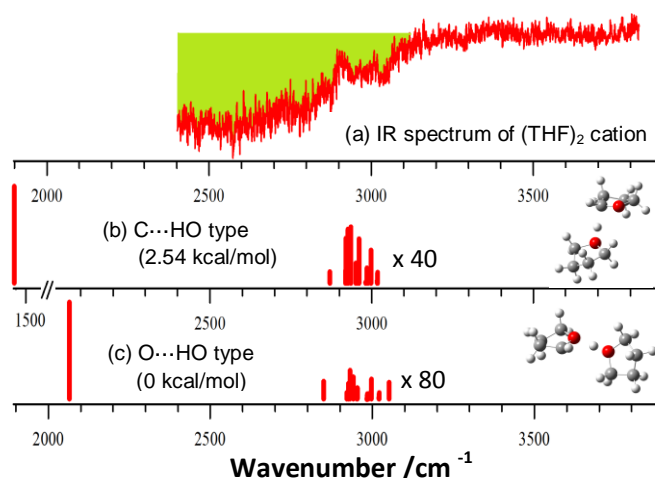


Figure 2. (a) Observed and (b, c) calculated IR spectra of the THF dimer cation and its two optimized structures.