

## 論文内容要旨

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学位論文の 題 目	<b>An Infrared Spectroscopic Study on Acidic CH Bonds in Cationic Ethers and Alkanes</b> (エーテル類及びアルカン類のカチオン状態における酸性 CH 結合に関する赤外分光研究)		

## 論文目次

<i>Acknowledgement</i> .....	I
<i>List of Figures</i> .....	V
<i>List of Tables</i> .....	VIII
<i>Introduction</i> .....	1
<i>Chapter 1 Proton transfer, gas phase acidity, and acidic bonds</i> .....	3
<i>Chapter 2 Methods</i> .....	18
<i>Chapter 3 Results and Discussion</i> .....	32
<i>Summary and outlook</i> .....	101

## 論文内容要旨

### Introduction and Chapter 1

Proton-transfer reaction is of fundamental importance in chemistry and biology. It often occurs in hydrogen-bonded systems which include some acidic X-H bonds. As well known, a hydrogen atom bounded to an atom of large electronegativity, such as N, O, S, and halogen atoms, is usually regarded as acidic (protic). In contrast, little attention has been paid to the role of CH bonds in proton-transfer reaction.

CH bonds are the most ubiquitous functional group in organic compounds. CH in a neutral molecule is normally regarded as aprotic because of its low acidity. On the other hand, though neutral OH and NH bonds are classified to weakly acidic sites, barrierless proton-transfer reactions from OH and NH bonds have recently been identified in ionized molecules.[1] This finding demonstrates that cationic OH and NH are highly acidic. Similar to cationic OH and NH, remarkable enhancement of the acidity of CH may be expected in the cationic state. In addition,

protonated products which would be formed through proton-transfer from CH are often seen in mass spectrometry of ion-molecule reactions. This also implies enhancement of the acidity of cationic CH.

In this study, we have studied the infrared (IR) spectroscopy of cationic cyclic ethers (tetrahydrofuran (THF) and tetrahydropyran (THP)) [2] and *n*-alkanes (pentane, hexane, and heptane), which are generated through the vacuum-ultraviolet (VUV) photoionization. The aim of this study is to investigate enhancement of the acidities of cationic CH bonds in these molecules and resulting proton-transfer from cationic CH. The mechanism of the acidity enhancement of cationic CH is explored through IR spectroscopic and theoretical investigation on the monomer and dimer cations.

## Chapter 2 Methods

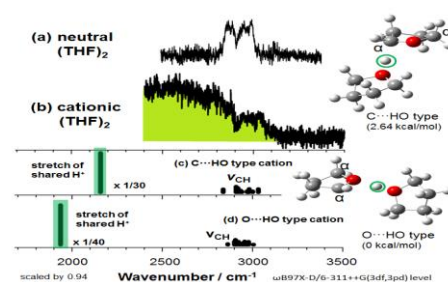
IR spectra of the cations of interest were observed by IR predissociation spectroscopy of VUV-pumped ions.[3] This is size-selective IR spectroscopy of the cations, which are generated with the VUV photoionization at 118 nm. The spectral measurements were performed by the principle of IR predissociation spectroscopy combined with size-selective detection of the parent or fragment ion by using mass spectrometric techniques.

In theoretical calculations, all the stable conformers were initially obtained from the global reaction route mapping (GRRM) program [4] at the PBE1PBE/6-31+G(d) level. Then, the optimized structures, energies, vibrational spectra, nature bond orbital (NBO), and spin density were re-calculated by the  $\omega$ B97X-D functional with the 6-311++G(3df, 3pd) basis set.

## Chapter 3 Results and Discussion

Figures 1(a) and 1(b) show the observed IR spectra of the neutral and cationic THF dimer, respectively, in the CH stretching vibrational region. In spectrum (b), a broad and intense feature appears from  $3100\text{ cm}^{-1}$  to the lower frequency region (which is highlighted by the shadow). This spectral feature is not seen in the spectrum of the neutral. Spectra (c) and (d) in Fig.1 are the simulated spectra based on the proton-transferred structures, which are the two most stable structures in the dimer cation. In these structures, the proton of the  $C_{\alpha}H$  bond is intermolecularly transferred to the oxygen atom and is shared by the two molecules. The observed broad feature is assigned to the stretch vibration of the shared proton of these isomers.

Figure 2 shows the potential energy curve obtained by the intrinsic reaction coordinate (IRC) calculation of the vertically-ionized THF dimer. As seen in the plot, no effective energy barrier exists in the proton-transfer route from the  $C_{\alpha}H$  bond in the ionized THF dimer. These results clearly indicate the CH bond in cationic THF is

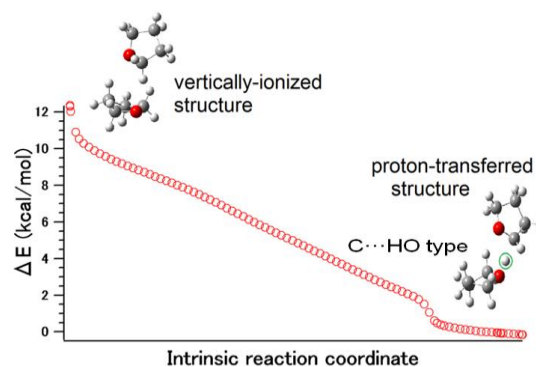


**Figure 1** Observed IR spectra of (a) neutral and (b) cationic THF dimer and (c, d) calculated IR spectra of the two most stable isomers of the dimer cation.

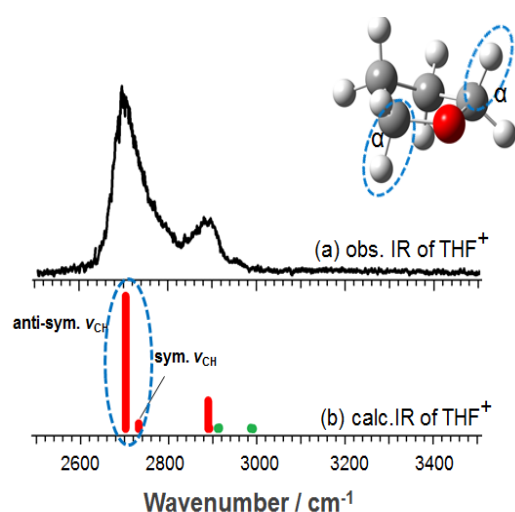
highly acidic.

Figure 3 shows the (a) observed and (b) simulated IR spectra for the stable structure (depicted in the figure) of the THF monomer cation. The observed intense band at  $2700\text{ cm}^{-1}$  is assigned to the anti-symmetric stretch vibration of the  $C_\alpha H$  bonds next to the oxygen atom. This band is clearly shifted to low frequency and its band position is out of the typical CH stretch frequency range of saturated hydrocarbons. The NBO analysis indicates that the high intensity and the low frequency of this band originate from the delocalization of the  $\sigma$  electrons of the  $C_\alpha H$  bonds to SOMO through the hyperconjugation. The delocalization of the  $\sigma$  electrons increases the positive charges of the hydrogen atoms of the  $C_\alpha H$  bonds and weakens their bond strengths, so that the proton donor ability of the  $C_\alpha H$  bonds is enhanced. Thus, this low frequency and highly intense band is a characteristic of the stretch vibration of the acidic CH bond in the cation.

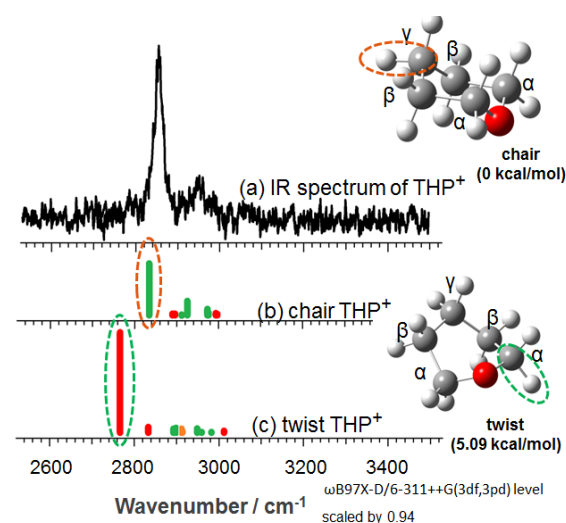
Tetrahydropyran (THP) is a six-membered ring ether, of which conformation is expected to be different from that of THF. Figure 4 shows (a) the observed IR spectrum of the cationic THP monomer and the calculated spectra for the (b) chair and (c) twist type structures inserted in the figure. Only these two structures are stable in the THP monomer cation. In the observed spectrum, an intense band is seen at  $2855\text{ cm}^{-1}$ . By comparison of the observed and calculated spectra, we assigned the spectral carrier 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  $\gamma$  position, indicated by the broken brown circle. The acidity of the  $C_\gamma H$  bond is enhanced because of delocalization of the bonding  $\sigma$  electron of  $C_\gamma H$  to the  $C_\alpha C_\beta$  bonds and SOMO of the oxygen atom through the hyperconjugation.



**Figure 2** Potential energy curve along the intrinsic reaction coordinate (IRC) of the vertically-ionized THF dimer cation at the  $\omega$ B97X-D/6-311++G(3df, 3pd) level.



**Figure 3** (a) Observed and (b) calculated IR spectra of the THF monomer cation. The calculated spectrum is based on the optimized structure at the  $\omega$ B97X-D/6-311++G(3df, 3pd) level. The calculated frequencies are scaled by 0.94.



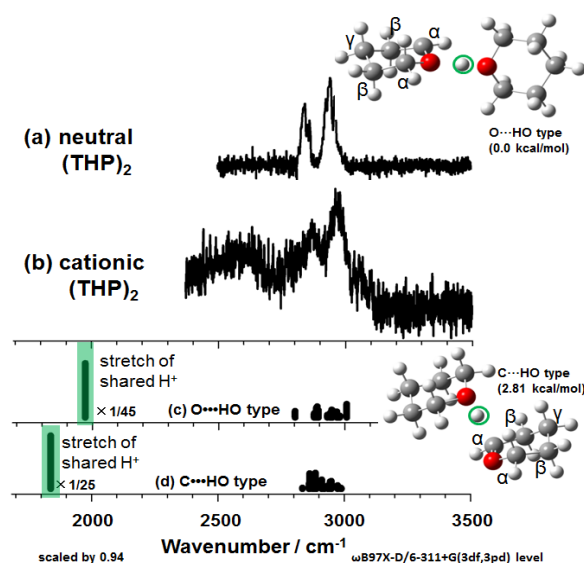
**Figure 4** (a) Observed IR spectrum of cationic THP and (b, c) calculated IR spectra of two optimized structures.

Figure 5 presents the observed IR spectra of the (a) neutral and (b) cationic THP dimers and (c)-(d) the simulated spectra of the two most stable structures of the dimer cation. In observed spectrum (b) of the dimer cation, CH stretch bands are seen in the range of 2800~3000  $\text{cm}^{-1}$  and a broad feature appears from 3100  $\text{cm}^{-1}$  to the lower frequency region. The latter band is not seen in the spectrum of the neutral dimer, and is explained by the stretching vibration of the shared proton in the two most stable structures of the O $\cdots$ HO and C $\cdots$ HO types. Both of the structures are formed through the intermolecular proton-transfer from the C $\alpha$ H next to the oxygen of the ionized moiety. This C $\alpha$ H acting as the proton donor is different from the acidic C $\gamma$ H in the THP monomer cation. This result implies the acidic site of the THP dimer cation switches from that of the bare cation in the proton transfer process.

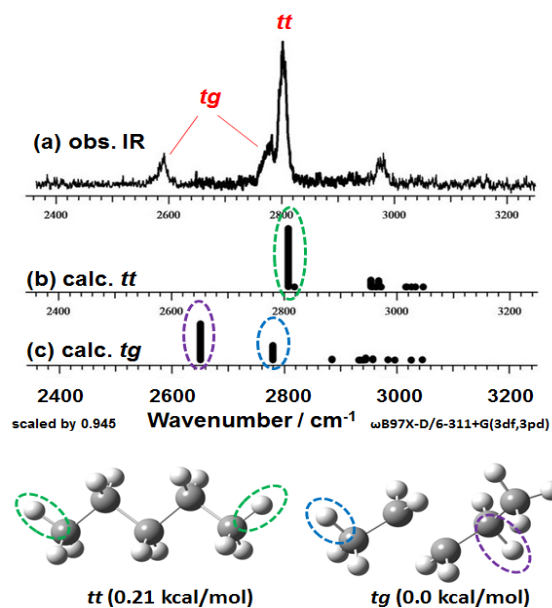
We carried out the IRC and GRRM calculations and the electron spin density distribution analysis on the THP dimer cation. We found that the proton transfer from C $\alpha$ H occurs with or without energy barrier depending on the initial geometry of the dimer cation. The mechanism for the acidic site switching and the details of the proton transfer process were discussed.

Different from the ethers, alkanes are composed only of carbon and hydrogen and have no non-bonding orbitals. To investigate the CH bond acidity in alkane cations, IR spectroscopy of *n*-alkane cations with different alkyl chain lengths (pentane, hexane and heptane) has also been performed.

Figure 6 shows (a) the observed IR spectrum of pentane cations and (b, c) the calculated IR spectra of the two most stable conformers, *tt* and *tg*, depicted in the figure. Comparison of the observed and calculated IR spectra indicates that the observed IR spectrum is attributed to both the two conformers. The most intense band labeled by *tt* is assigned to the stretches of the in-plane (the plane is composed of the five carbon atoms) CH bonds at the ends of the *tt*



**Figure 5** Observed IR spectra of (a) neutral and (b) cationic THP dimers and (c, d) calculated IR spectra of two optimized structures of the dimer cation.

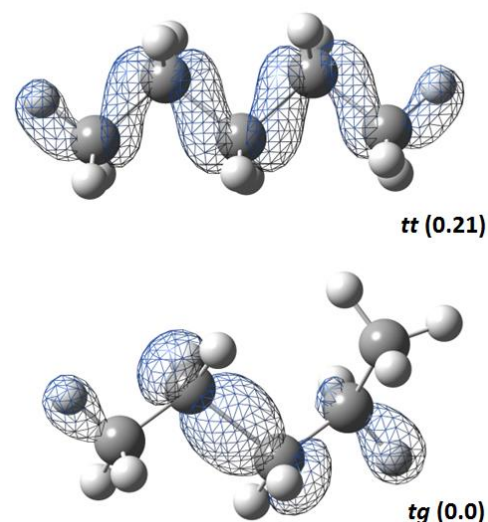


**Figure 6** (a) Observed IR spectrum of pentane cations and (b, c) calculated IR spectra of the two most stable conformers together with their structures.

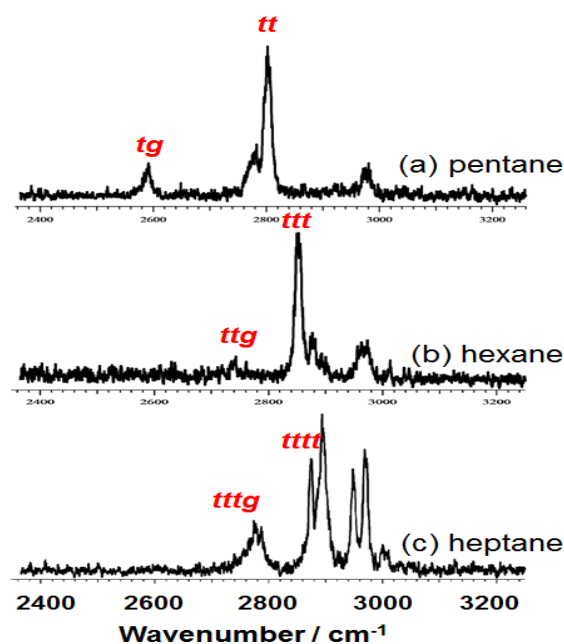
conformer (highlighted by the green circles). The band at  $\sim 3000\text{ cm}^{-1}$  is assigned to the stretch bands of the out-of-plane CH bonds of both the isomers. The two low frequency CH bands labeled by *tg* belong to the *tg* conformer. The lowest frequency band is assigned to the in-plane CH bond (highlighted by the purple circle) next to the out-of-plane methyl group, and the other band is assigned to the in-plane CH bond (highlighted by the blue circle) at the end of the *tg* conformer. These low frequency bands below  $2850\text{ cm}^{-1}$  indicate the acidity enhancement of the CH bonds also occurs in cationic pentane. The frequencies of the two lowest frequency bands of the *tg* conformer are lower than that of the intense *tt* band, which is the lowest frequency CH stretch band in the *tt* conformer. This indicates that the CH bonds in the *tg* conformer are more acidic than those of the *tt* conformer.

To investigate the origin of the different acidities of the *tt* and *tg* conformers, the spin density analysis of these two conformers has been performed and the result is shown in Figure 7. The spin density represents the delocalization of the positive charge in the cation. As we can see in the figure, the positive charge mainly delocalizes on the in-plane CC and CH bonds in both the conformers. The spin density indicates the hole density in the bonding orbital, and its magnitude should be a measure of the bond weakening. In the *tt* conformer, the spin density delocalizes more widely in the in-plane orbitals of the whole molecule than that of *tg* conformer. In this case, the positive charge density at the in-plane CH bonds of the *tt* conformer should be lower than that of the *tg* conformer, and the bond weakening in the *tt* conformer is less than that of the *tg* conformer. Therefore, the in-plane CH bond in the *tg* conformer is more acidic than that of the *tt* isomer. This result demonstrates that the acidities of the CH bonds in the cationic pentane correlate with its conformation, which affects through the delocalization of the positive charge.

The similar trend on the acidity enhancement of CH was seen for cationic hexane and heptane. Many isomers were found to coexist also in these cations. The mechanisms of their acidity enhancements were analyzed based on the experimental and theoretical results.



**Figure 7** The spin density (isoval = 0.007) of the *tt* and *tg* isomers of cationic pentane.



**Figure 8** IR spectra of cationic pentane, hexane, and heptane.

To investigate the correlation between the acidity of the CH bond and the length of the alkyl chain, we compared the IR spectra of cationic pentane, hexane, and heptane, which are shown in Figure 8. The relatively intense bands that labeled as *tt*, *ttt*, and *tttt* in the spectra are attributed to the all *trans* conformers of the three alkane cations. The low frequency bands which labeled as *tg*, *ttg*, and *tttg* are attributed to the conformers with an out-of-plane CH<sub>3</sub> group in the end of the molecule. The frequencies of both the types of the CH bands are obviously blue shifted with increasing alkyl chain length. This indicates their acidities decrease with increasing alkyl chain length.

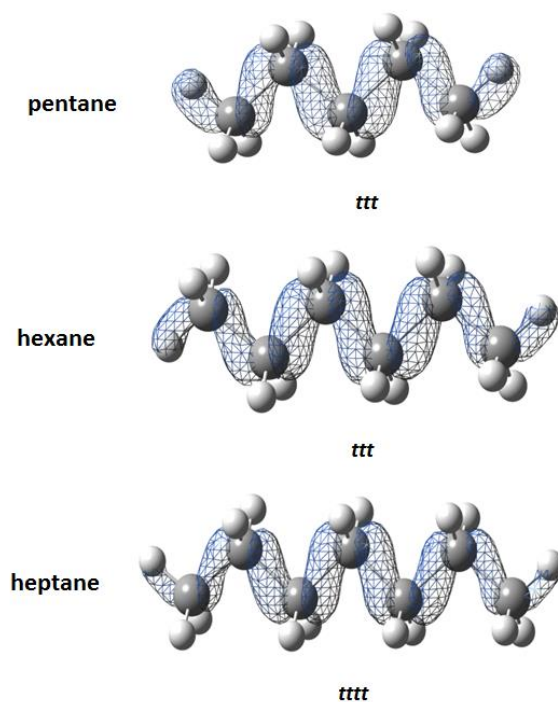
As a typical example, Figure 9 shows the spin density of the all *trans* conformers of cationic pentane, hexane, and heptane. As we can see in their spin density, the positive charge is shared by all the in-plane orbitals (the CC bonds and two CH bonds at the end of the chain). Thus, the chain length becomes longer, the spin density (positive charge density) at the CH bonds becomes lower and then their acidity also less. The blue shift trend seen in the conformers with an out-of-plane CH<sub>3</sub> group is due to the same mechanism.

The gas phase acidities of these species also have been calculated, and they are consistent with the present experimental results.

The present study of the cationic cyclic ethers (THF and THP) and *n*-alkanes (pentane, hexane, and, heptane) indicates the cationic CH bonds are highly acidic and IR spectroscopy of CH bonds is useful to examine their acidities.

## References

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- [2] M. Xie, Y. Matsuda, A. Fujii, *J. Phys. Chem. A* **119**, 5668 (2015).
- [3] Y. Matsuda, N. Mikami, A. Fujii, *Phys. Chem. Chem. Phys.* **11**, 1279 (2009).
- [4] K. Ohno and S. Maeda, *Chem. Phys. Lett.* **384**, 277 (2004).



**Figure 9** The spin density (isoval = 0.007) of the all *trans* conformers of cationic pentane, hexane, and heptane.



## 論文審査の結果の要旨

水素結合に代表される分子間相互作用は集合体としての物質の化学的性質を決定づける要因であり、非常に数多くの研究の蓄積がなされてきている。しかしながら、その大半は中性状態における知見であり、カチオン状態における分子間相互作用には未解明の事項が多い。しかしカチオン種の実験研究における多くの困難のため、これまでその研究例は限られてきた。

これに対し本研究は、基本的なエーテル類およびアルカン類分子のラジカルカチオンに着目し、そのC H結合の酸性度（プロトン授与能力）がイオン化により劇的に上昇し、更にその強度が分子のコンフォメーションに強く依存することを示した。具体的には、孤立気相条件下での中性、カチオン状態におけるC H伸縮振動の観測を赤外分光により行い、密度汎関数法による解析との比較から、以下の知見を得た。（１）テトラヒドロフラン（THF）ではイオン化により酸素原子に隣接する $\alpha$ 位のC H結合の酸性度が顕著に増大し、そのためTHF二量体ではイオン化に伴ってC Hからのプロトン移動が起きる。（２）テトラヒドロピラン（THP）では、同じくイオン化に伴いC H結合の酸性度増大が生じるが、それが生じるのは酸素原子から離れた $\gamma$ 位のC H結合になる。THP二量体においてもイオン化に伴うC H結合からのプロトン移動が起きるが、移動の過程で分子のコンフォメーション変化が起き、これにより酸性となるC H結合部位が $\alpha$ 位に変わり、そこからのプロトンが移動する。（３）これらのC H結合の酸性度の増加はC H結合と酸素原子を中心とする半占軌道との相互作用（超共役）によるものである。超共役の強さは軌道の重なりによって支配されるため、酸性となるC H結合部位が分子のコンフォメーションを鋭敏に反映する。（４）アルカン類分子のラジカルカチオンにおいてもC H結合の顕著な酸性度上昇が生じ、コンフォメーション依存性が確認された。

これらの結果は真空紫外光イオン化検出を用いた赤外分光という先端分光計測技術を駆使して得られたものであり、非常に高度な実験技術の結実である。本論文はラジカルカチオンにおけるC H結合の性質が中性のそれとは根本的に異なることを実験・理論の両面で証明しており、その意義は大きい。本論文は謝敏氏が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、謝敏氏提出の博士論文は、博士（理学）の学位論文として合格と認める。