

Infrared spectroscopic investigation of CH bond acidity in cationic alkanes

(Tohoku Univ.) ○Min Xie, Yoshiyuki Matsuda, Asuka Fujii

[Introduction] CH bonds are the most ubiquitous functional group in organic compounds. CH in a neutral molecule is generally regarded as aprotic because of its low acidity. Recently, we have demonstrated the CH bonds in the cationic ethers [1, 2] and amines [3] are highly acidic. In these cations, the acidities of CH bonds are enhanced through the hyperconjugation of the CH bond with the nonbonding orbital which is the singly occupied molecular orbital (SOMO). Alkanes are composed only of carbon and hydrogen and have no nonbonding orbital. In the ionization process to their cationic ground state, a σ electron is ejected. For alkane cations, therefore, we have had a question whether their CH bonds undergo acidity enhancements without the nonbonding orbital or not. In this study, to investigate the CH bond acidity in alkane cations, we perform infrared (IR) spectroscopy of *n*-alkane cations with different alkyl chain lengths (pentane, hexane, and heptane).

[Experiments and Calculations] IR spectra of Ar⁻ or N₂-tagged alkane cations were observed by IR predissociation spectroscopy of VUV-pumped ions. In this spectroscopy, the tagged alkane cations were generated through the VUV photoionization at 118 nm. We used a tandem-type quadrupole mass (Q-mass) spectrometer to perform IR dissociation spectroscopy. The generated tagged cations were size-selected through the first Q-mass filter. The IR predissociation spectrum of the size-selected cation was recorded by monitoring the bare cation intensity through the second Q-mass filter.

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

[Results and Discussion] Figure 1 shows (a) the observed IR spectrum of pentane cations and (b, c) the calculated IR spectra of the two stable conformers, *tt* and *tg*, depicted in the figure. Comparisons of the observed and calculated IR spectra indicate that the observed IR spectrum is attributed to the two conformers. The most intense band labeled by *tt* is assigned to the stretches of the in-plane (the plane is composed by the five carbon atoms) CH bonds in the

terminals of the *tt* 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. 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 terminal in-plane CH bond (highlighted by the blue circle) of the *tg* conformer. These low frequency bands below 2850 cm^{-1} indicate the acidity enhancement of the CH bonds occurs in cationic pentane. The CH bonds assigned to these low frequency bands are influenced by delocalization of the positive charge. Therefore, the C-H bonds are weakened and the enhancement of their acidities is also caused. The frequencies of the two low frequency bands of the *tg* conformer are lower than that of the intense *tt* band, which is the lowest CH stretch band in the *tt* conformer. This indicates that the CH bonds highlighted by the blue and purple circles in the *tg* conformer is more acidic than the in-plane CH bonds at the terminals of the *tt* conformer. Thus, the acidities of the CH bonds in the cationic pentane correlates with its conformation, which affects the delocalization of the positive charge.

We will discuss the detailed mechanisms of the acidity enhancement of the CH bonds in the cationic alkanes, the correlations between the CH bond acidities and conformations, and the dependence of the alkyl chain length on their acidity, based on the IR spectra and theoretical calculation results on preferable geometries, vibrational simulations, and spin density distributions.

[References]

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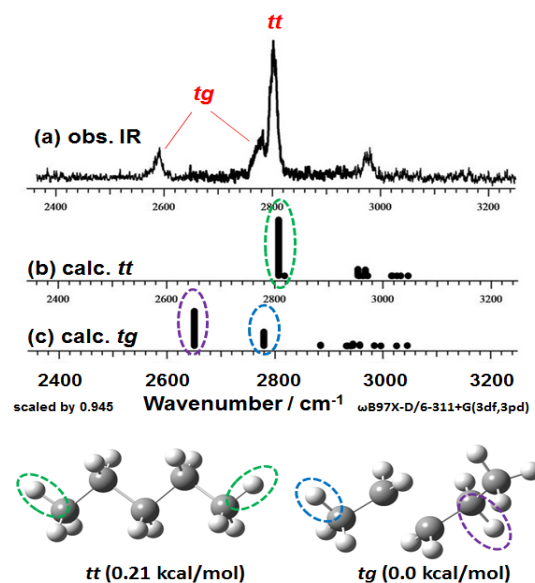


Figure 1 (a) The observed IR spectrum of pentane cations and the (b, c) the calculated IR spectra of the stable conformers shown the figure.