# Protomer identification by IR spectroscopy combined with collision assisted stripping technique in cryogenic ion trap

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If a molecule has several basic sites, several isomers in which the protonated positions are different can exist. Such isomers are called protomer. Since the charge on the molecule significantly affects its properties; structure, reactivity, etc., it is crucial to know which protomer abundantly exists. In addition, the protomer abundance is significantly affected by hydration. For example, *p*-amino benzoic acid (PABA) has two protomers; one is N-protomer in which the amino group is protonated, and another is O-protomer in which the oxygen atom of the carboxy group is protonated. In aqueous solution, only the N-protomer exist, while the O-protomer is favorable in dehydrated state, such as in gas phase. Thus, by stepwise hydration on the isolated PABA, the O-protomer should switch to the N-protomer. In fact, Williams and co-workers reported such protomer switching by stepwise hydration.[1] They measured IR photo dissociation (IRPD) spectra of size-selected hydrated clusters of protonated PABA ($PABAH^+(H_2O)_n$), and revealed that the N-protomer appears in $n$=6. However, since they measured NH and OH stretching region, the presence of the N-protomer in the $n$=1–5 spectra is not clear because of the spectral congestion of H-bonded OH stretch of many isomers, as stated by the authors. In addition, even if the spectrum is highly resolved, existence or nonexistence of the protomers can be concluded, but the protomer abundance is hardly estimated quantitatively.

To overcome this problem, we developed a new technique, collision assisted stripping IR spectroscopy (CAS-IR), which enables us to precisely determine the protomer abundance in highly hydrated clusters. In this method, size-selected hydrated cluster ion is injected with high kinetic energy to a cryogenic ion trap in which He buffer gas is introduced. By the collision with the cold He gas, water molecules of the hydrated cluster are eliminated and the bared ion is trapped. Here, hydrogen gas is introduced and hydrogen attached ion (tagged ion) is generated. Then, IRPD spectroscopy can be performed by monitoring the hydrogen detaching due to IR absorption. Since the protomers of the bared ions can be clearly identified by IR spectra, we can easily determine which protomer is included in the hydrated cluster before the CAS process, and estimate the protomer abundance, if proton transfer does not occur during the CAS process.

In this work, we apply the CAS-IR technique to benzocaine[2], PABA, several nicotine derivatives[3], etc. By measuring benzocaine, we confirmed the quantitativeness of the method. The detail of the CAS-IR technique and several applications will be introduced.

References:
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