Research paper

Infrared spectroscopic evidence for the initial step of dissociation of the stable benzoic acid cyclic dimer with microsolvation by a single water molecule

Marusu Katada, Asuka Fujii *

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

ABSTRACT

The hydrogen-bonded structure of the (Benzoic acid)$_2$-(Water)$_1$ (BA$_2$-W$_1$) cluster was investigated by infrared spectroscopy in the OH stretch region. The stable BA dimer has the cyclic structure with the two hydrogen bonds between the carboxyl groups. The observed infrared spectrum of BA$_2$-W$_1$ shows that the water molecule is inserted in between the two carboxylic groups of the cyclic dimer. This means that a single water molecule begins to dissociate the cyclic dimer. This observation can be regarded as the initial step of dissociation of the stable cyclic BA dimer in aqueous solution.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Benzoic acid (BA) is the most fundamental aromatic carboxylic acid. It has been known that BA forms a stable cyclic dimer (BA$_2$) with two OH···O=C hydrogen bonds (H-bonds) between the carboxylic groups. The binding energy of BA$_2$ is estimated about 15 kcal/mol in the gas phase [1,2]. This dimer structure is highly stable, and therefore, it is observed not only in low temperature supersonic jet and crystalline structure but also under warm conditions such as solution and room temperature vapor [3]. To act as an acid in diluted aqueous solution, however, this cyclic dimer should dissociate to two monomers with hydration.

Though the cyclic structure of BA$_2$ has been confirmed by infrared (IR) spectroscopy under the jet-cooled condition [3–5], H-bonded structures of micro-hydrated BA$_2$ have been examined only by quantum chemical calculations [6–11]. The computations by Sagarik et al. have suggested that in this micro-hydration, even a single water molecule is inserted into the H-bonded ring of the dimer and the three molecules form a larger H-bonded ring [9,10]. Though this structure of the BA$_2$-(H$_2$O)$_1$ (BA$_2$-W$_1$) cluster can be regarded as the initial step of the dissociation of the cyclic dimer with the hydration, other stable structures, in which the water molecule solvates the cyclic dimer at the outside of the H-bonded ring, were also found in the theoretical calculations. For BA$_2$-W$_n$ clusters, an electronic spectrum under the supersonic jet

condition has been reported by Tomioka et al. [12]. On H-bonded structures of these BA$_2$-W$_n$ clusters, however, no direct experimental evidence has been reported.

IR spectroscopy in the OH stretch region is a very powerful tool for investigation of H-bonded structures. Among clusters of BA, only an IR spectrum of BA$_2$ in the OH stretch region has been reported [3]. In the present study, to explore the initial hydration process of BA$_2$, we measure an IR spectrum of the BA$_2$-W$_1$ cluster and demonstrate that a single water molecule begins the dissociation process of BA$_2$. In addition, we calculate the energy levels of the singlet and triplet excited states of hydrated BA clusters using time-dependent density functional theory (TD-DFT) and discuss on their decay process and ionization efficiency.

2. Experiment and calculation

The sample of BA was purchased from KANTO CHEMICAL CO., and was used without further purification. A pulsed supersonic jet nozzle (General Valve series 9) was heated to about 380 K to increase the vapor pressure of the sample. The BA$_2$-W$_1$ cluster was generated by a supersonic jet expansion of a gaseous mixture of BA, water, and He. The stagnation pressure of the gas was about 3 atm. The jet expansion was skimmed to form a molecular beam. An electronic spectrum of the BA$_2$-W$_1$ cluster has been measured by the laser induced fluorescence detection [12], but we re-measured the spectrum by the two-color resonance-enhanced multiphoton ionization (REMPI) method combined with mass spectrometry to clearly identify the spectral carrier. Two ultravio-

* Corresponding author.
  E-mail address: asukafujii@m.tohoku.ac.jp (A. Fujii).

let (UV) pulsed lasers (ν_1 and ν_2) were introduced into the interaction region from the perpendicular direction to the molecular beam. The ν_1 laser excited the BA moiety of the of BA_2-W_1 cluster to the $^1\pi\pi^*$ state and the ν_2 laser (240 nm) successively ionized the cluster in the excited state without time delay. The generated ions were mass-selected by a Wiley–McLaren type time-of-flight mass spectrometer and were detected.

An IR spectrum of the BA_2-W_1 cluster was observed by IR–UV double-resonance spectroscopy [13]. A tunable IR laser pulse was introduced 50 ns prior to the UV laser pulses. The ion intensity decreases when the cluster absorbs the IR light because of the reduction of the vibrational ground level population. Therefore an IR spectrum was observed by monitoring the ion intensity while scanning the IR frequency.

Quantum chemical calculations were also performed to search stable structures of the cluster. Initial structure search was performed at the B3LYP/6-31+G(d) level. The searched stable structures were re-optimized at the MP2/cc-pVDZ level, and the relative energies with the zero-point energy correlation and harmonic vibrational frequencies were evaluated. These computations were performed by Gaussian 09 [14]. It has been shown that the OH stretching band structure of BA_2 is very complicated because of the anharmonic coupling with OH bending and intermolecular vibrations [3]. In order to analyze the measured IR spectrum of BA_2-W_1, anharmonic vibrational calculations were also performed by the vibrational second-order perturbation theory (VPT2) method [15] using Gaussian 16 [16]. To reduce computational cost, the anharmonic vibrational calculations were performed only for the most stable structure of BA_2-W_1. To estimate the decay process in the excited state, TD-DFT calculations were performed at the UB3LYP/6-31+G(d) level. The TD-DFT calculations [17] were performed using the MP2 level structures by Gaussian 16.

3. Results and discussion

Fig. 1 shows the REMPI spectra of BA_2-W_n clusters. Spectra (a), (b), (c), and (d) were observed by monitoring $(BA_2$-$W_2)^+$, $(BA_2$-$W_1)^+$, $(BA_2$-$W_1)^+$ (2 h after the measurement of (b)), and $(BA_2)^+$, respectively. The band features of spectrum (d) are similar to those previously measured by the fluorescence detection [12,18,19] and REMPI detection [4]. The strongest band in spectrum (d) is assigned to the 0–0 band of the $\pi\pi^*$ transition of BA_2 and most of other sharp bands which appear in the blue side are attributed to its vibronic bands [4,12]. We also observed a REMPI spectrum by monitoring BA^+. However, no band originating from the monomer was observed and the observed spectrum was exactly same as spectrum (d). This may be caused by the following two reasons. One is that an abundance of the BA monomer is much smaller than BA_2 under the jet-cooled condition [4]. Another reason is that the ionization efficiency of the monomer is very low because its lifetime of the S_2 ($\pi\pi^*$) state is short due to the fast internal conversion to S_1 ($n\pi^*$) and following efficient intersystem crossing from S_1 to T_n states [4,8].

Tomioka et al. have assigned the strongest band (35,872 cm^{-1}) in spectrum (b) to BA_1-W_n clusters [12]. However, the present REMPI measurement indicates that this band is attributed to BA_2-W_1 cluster. The intensity distribution of spectrum (b) is very different from that in the previous fluorescence excitation spectrum. The bands at 35,806 and 35,907 cm^{-1} are absent and the band at 35,622 cm^{-1} is much stronger than the band at 35,872 cm^{-1} in the fluorescence excitation spectrum [12]. This band intensity behavior suggests coexistence of isomers of BA_2-W_1. The difference between the intensity distributions of the fluorescence excitation and REMPI spectra would originate from difference of the fluorescence quantum yield and ionization efficiency among the isomers. In addition, the isomer distribution also depends on the jet expansion condition.

Spectrum (c) was measured about 2 h after the measurement of spectrum (b). The relative intensity of the band at 35,806 cm^{-1} clearly decreases though the measurement condition was not changed. This suggests that the carrier of the 35,806 cm^{-1} band is an isomer less stable than that of the 35 872 cm^{-1} band. Spectrum (a) by monitoring $(BA_2$-$W_2)^+$ shows only the broad features. This would reflect the fast relaxation process in BA_2-W_2 in the $S_2(\pi\pi^*)$ state. We will discuss on this issue later.

Fig. 2(a) shows the IR spectrum measured by probing the band at 35,872 cm^{-1} in spectrum (b) of Fig. 1. The gap at around 3500 cm^{-1} is due to the IR absorption by the nonlinear optical crystal used for the difference frequency generation. The band structure of the IR spectrum is obviously complicated due to the
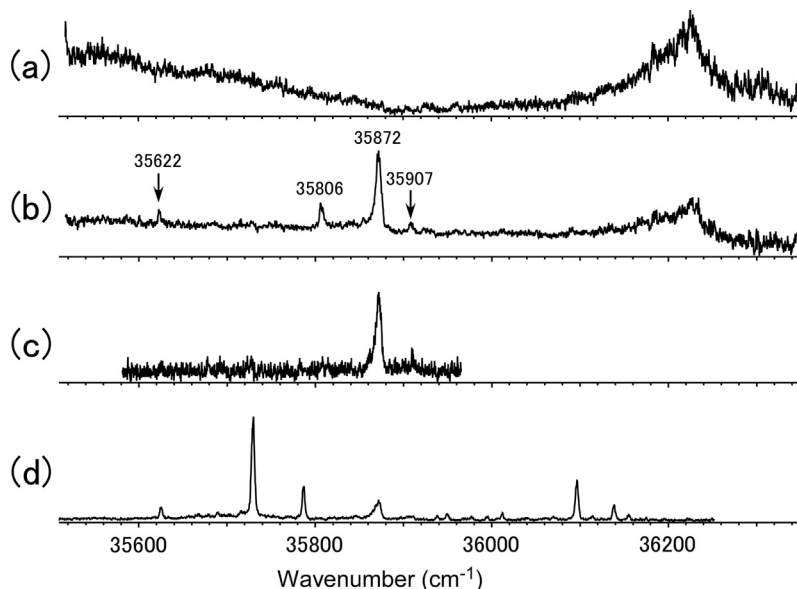

Fig. 1. Resonance-enhanced multiphoton ionization (REMPI) spectra measured by monitoring (a) BA_2-W_2^+, (b) BA_2-W_1^+, (c) BA_2-W_1^+ (2 h after the measurement of spectrum (b)), and (d) BA_2^+.