Infrared photodissociation spectroscopy of protonated formic acid and acetic acid clusters

Yoshiya Inokuchi and Nobuyuki Nishi[*]

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Abstract

Infrared spectra of protonated carboxylic acid clusters, $H^+\bullet(HCOOH)_n$ and $H^+\bullet(CH_3COOH)_n$ (n = 2–5), are measured by infrared photodissociation spectroscopy. Density functional theory calculation is applied to $H^+\bullet(HCOOH)_{2-5}$. Similarity of the spectra between $H^+\bullet(HCOOH)_n$ and $H^+\bullet(CH_3COOH)_n$ suggests that only the COOH group is involved in intermolecular bond formation. The n = 2 and 3 ions have two sharp bands in the range of 3400–3700 cm^{-1}. These bands are assigned to the free OH stretching vibrations of the *E* and *Z* conformations at the ends of chain structures. The band of the *Z* conformation decreases its intensity from n = 2 to 3 and disappears for n = 4 and 5. The *Z* conformation at the ends becomes unstable with increasing cluster size. We also observe infrared spectra of $H^+\bullet(HCOOH)_n$ (n = 6 and 7) in the 3500–3600 cm^{-1} region. The absence of the free OH band in the spectrum of n = 7 confirms that both ends of the chain structure are terminated by cyclic dimers in the n = 7 ion.

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[*] Corresponding Author. e-mail:nishi@ims.ac.jp

1. Introduction

Carboxylic acid (RCOOH) is one of the popular acids in organic chemistry. A number of researches have been devoted to clarify intermolecular configurations of carboxylic acid.[i–xi] In crystals, carboxylic acid molecules are interlinked to form either a cyclic dimer or an infinite chain; the linkage manner depends on the substituent R.[1] Formic acid molecules form an infinite chain in the crystal[1] and a cyclic dimer in the gas phase.[11] Lifshitz and co-workers have extensively investigated protonated carboxylic acid clusters.[xii – xv] They created the clusters by the electron-impact ionization and observed the unimolecular dissociation.[12, 13] The $H^+\bullet(RCOOH)_n$ clusters with $n \leq 5$ release a neutral monomer. A neutral dimer is also evaporated from the clusters larger than $n = 5$. They carried out ab initio calculations and obtained stable structures of the clusters.[14] Open-chain structures are favored energetically for $n \leq 5$; there is at least one free OH bond at the periphery. Chain structures terminated by cyclic dimer units are preferable for $n \geq 6$. The calculated results well corroborated the experimental results.[12, 13]

Vibrational spectroscopy is one of the most powerful methods to determine structures of molecules and clusters. In particular, infrared photodissociation spectroscopy is quite useful for cluster ions.[xvi – xx] By measuring infrared photodissociation spectra, one can obtain vibrational frequencies and discuss cluster structures. We applied this spectroscopy to the protonated formic acid–water binary clusters, $H^+\bullet(HCOOH)_{1-5}\bullet H_2O$.[xxi] The $H^+\bullet(HCOOH)_5\bullet H_2O$ ion has the ring structure that surrounds an H_3O^+ ion core.

In this paper, we report structures of $H^+\bullet(HCOOH)_n$ and $H^+\bullet(CH_3COOH)_n$ (n = 2–5). Infrared photodissociation spectra of the clusters are measured by use of an ion guide spectrometer and a pulsed infrared laser. Geometries of the clusters are optimized and vibrational frequencies are evaluated by density functional theory (DFT) calculation. The stability of the E and Z conformations of the COOH group is discussed from the band intensities.[xxii] For the formic acid system, we extend the measurement to $n = 7$ for investigating the termination manner of chain structures.

2. Experimental and computational

The infrared photodissociation spectra of $H^+\bullet(HCOOH)_n$ and $H^+\bullet(CH_3COOH)_n$ are measured by use of an ion guide spectrometer with two quadrupole mass filters.[xxiii] Gas mixture of carboxylic acid and argon is introduced into a vacuum chamber through a pulsed nozzle (General Valve Series 9) with a 0.80 mm orifice diameter . The total stagnation pressure is 1×10^5 Pa. Neutral clusters are ionized by an electron-impact ionizer situated near the exit of the pulsed nozzle. The electron kinetic energy is adjusted to 350 eV. After passing through a skimmer, cluster ions are introduced into the spectrometer. Parent ions are isolated by the first quadrupole mass filter. After deflection by 90° through an ion bender, the parent ions are led into a quadrupole ion guide. The ion beam is merged with a laser beam in the ion guide, and the parent ions are excited into vibrationally excited states. The excitation induces fragmentation of the parent ions. Resultant fragment ions are mass-analyzed by the second quadrupole mass filter, and detected by a secondary electron multiplier tube. For normalization of the fragment-ion yield, the power of the dissociation laser is monitored by a pyroelectric detector (Molectron P1-15H-CC). Infrared photodissociation spectra of the parent ions are obtained by plotting the normalized yields of the fragment ions against wavenumber of the dissociation laser. The fragment ion detected is $H^+\bullet(RCOOH)_{n-1}$ for the spectra of $H^+\bullet(RCOOH)_n$.

The tunable infrared source used in this study is an optical parametric oscillator (OPO) system (Continuum Mirage 3000) pumped with an injection-seeded Nd:YAG laser (Continuum Powerlite 9010). The output energy is 1–2 mJ/pulse, and the linewidth is approximately 1 cm^{-1}.

Moreover, the H^{+}•$(HCOOH)_n$ (n = 2–5) clusters are analyzed by DFT calculation. The calculations are made with the Gaussian 98 program package.[xxiv] Geometry optimization and vibrational frequency evaluation are carried out at the B3LYP/ 6-31++G(d,p) level of theory. The calculations at this level have been successful for protonated formic acid–water binary clusters.[21]

3. Results and discussion

A. H^{+}•$(HCOOH)_n$ (n = 2–7)

Figure 1 shows the infrared photodissociation spectra of (a–d) H^{+}•$(HCOOH)_n$ with n = 2–5. The n = 2 and 3 ions have two sharp bands in the range of 3400–3700 cm^{-1}. For the n = 4 and 5 ions, only one sharp band emerges in the same region. Bands in this region are assigned to the free OH stretching vibration of the COOH group. Table 1 collects band positions of the spectra. In the 3000–3400 cm^{-1} region of the n = 3 spectrum, there is an absorption that increases more and more with decreasing frequency. A broad band with a maximum around 3230 cm^{-1} appears for the n = 4 and 5 ions.

Optimized structures of HCOOH and H^{+}•$(HCOOH)_n$ (n = 1–5) are shown in Fig. 2. For calculations of these species, we refer substantially to the calculations done by Zhang and Lifshitz.[14] They mentioned that open-chain structures are favored energetically for H^{+}•$(HCOOH)_n$ with $n \leq 5$. In this study, therefore, we calculate open-chain structures of the formic acid clusters, and focus our attention on the stability of the *E* and *Z* conformations of the COOH group at the periphery. The neutral formic acid molecule has the *E* conformation (Fig. 2a).[xxv] In the $n = 1$ ion, there are both the *E* and *Z* conformations (Fig. 2b). Two stable structures are displayed for $n = 2$ (Figs. 2c and d). In the most stable structure, a proton is equally shared by two molecules that have the *E* conformation (Fig. 2c). This structure was not obtained in the previous study.[14] The second most stable isomer has an $HCOOH_2^+$ ion core (Fig. 2d). A solvent molecule is bound to the *Z* site of the ion core, similar to the structure of $HCOOH_2^+{\bullet}H_2O$.[21] The solvent molecule has the *Z* conformation. The most stable structure of $n = 3$ has the *E* and *Z* conformations at the periphery (Fig. 2e). The second most stable form has the *E* conformations at both ends (Fig. 2f). For the $n = 4$ and 5 ions, on the other hand, conformations at the ends are *E* type in the most stable structures, as shown in Figs. 2g and h. Hereafter, we call the cluster form that has the *E* and *Z* conformations at the periphery an (*E*, *Z*) isomer.

Vibrational frequencies of the optimized structures are listed in Table 1. For the isomers of $n = 2$, the free OH stretching bands of the *E* conformation are predicted at 3505, 3506, and 3499 cm^{-1}. The free OH stretching frequency of the *Z* conformation is calculated to be 3572 cm^{-1}. These values are well coincide with the observed values (3489 and 3565 cm^{-1}). Therefore, we assign the bands observed at 3489 and 3565 cm^{-1} to the free OH stretching vibrations of the *E* and *Z* conformations, respectively. The appearance of the band of the *Z* conformation suggests that there is the (*E*, *Z*) isomer (Fig. 2d) in our experiment. An intensity of the 3565 cm^{-1} band relative to that of the 3489 cm^{-1} band is 0.45. For the (*E*, *Z*) isomer, infrared intensities of the OH stretching vibrations of the *E* and *Z* sites are 174 and 211 km/mol; the relative intensity is 1.2. The (*E*, *E*) isomer (Fig. 2c) is necessary for explaining the relative band intensity observed. On the basis of the intensities observed and calculated, we estimate a relative abundance of the (*E*, *Z*) and (*E*, *E*) isomers. If the two isomers equally contribute to the infrared spectrum, the relative intensity of the *E* and *Z* conformations is 211/(331 + 0 + 174) = 0.42 (see Table 1). This value is almost the same as the relative intensity observed in the infrared spectrum (0.45). Therefore, there are almost equal amounts of the (*E*, *Z*) and (*E*, *E*) isomers in our ion source.

The (*E*, *Z*) isomer of $n = 3$ (Fig. 2e) has the free OH stretching vibrations of the *E* and *Z* conformations at 3529 and 3585 cm^{-1}. The infrared spectrum of $n = 3$ shows two bands at 3532 and 3600 cm^{-1}. The band positions observed and calculated are close to each other. The 3532 and 3600 cm^{-1} bands are ascribed to the free OH stretching vibrations of the *E* and *Z* conformations. An intensity of the 3600 cm^{-1} band relative to that of the 3532 cm^{-1} band is 0.25. On the other hand, intensities of the *E* and *Z* conformations are calculated to be 115 and 168 km/mol for the (*E*, *Z*) isomer; the relative intensity is 1.5. Introduction of the (*E*, *E*) isomer (Fig. 2f) resolves the discrepancy. Estimation from the intensities calculated and observed suggests that the (*E*, *E*) isomer is 2.6 times more abundant than the (*E*, *Z*) isomer.

The tendency of the relative stability between the (*E*, *E*) and (*E*, *Z*) isomers is quite remarkable for the $n = 4$ and 5 ions. The infrared spectra of the $n = 4$ and 5 ions have only one sharp band at 3547 and 3545 cm^{-1}, respectively. Average values of the estimated frequencies of the free OH stretching vibrations are 3542 and 3547 cm^{-1} for the (*E*, *E*) isomers of $n = 4$ and 5; these values coincide well with the observed ones. Therefore, the observed bands are assigned to the free OH stretching vibrations of the *E* conformation. No band of the *Z* conformation is observed, suggesting that the $n = 4$ and 5 ions have only the (*E*, *E*) isomers.

The observed frequencies of the free OH stretching of the *E* conformation increase with increasing cluster size (3489, 3532, 3547, and 3545 cm^{-1} for $n = 2–5$). The values of the $n = 4$ and 5 ions are close to that of neutral formic acid (3550.5 cm^{-1}).[25] The calculations show a similar trend; average values of the *E* conformation are 3503, 3535, 3542, and 3547 cm^{-1} for $n = 2–5$. The increase of the frequency is originated from the decrease of the charge on the end molecules. According to the calculation results, average charges on the end molecules that have the *E* conformation are 0.872, 0.084, 0.054, and 0.039 for the $n = 2–5$ ions, respectively. The decrease of the charge also affects the relative stability between the *E* and *Z* conformations. The $n = 1$ ion has the (*E*, *Z*) conformation, as shown in Fig. 2b. For $n = 2$ and 3, both the (*E*, *Z*) and (*E*, *E*) isomers coexist in our experiment; the abundance of the latter isomer increases from $n = 2$ to 3. In the case of $n = 4$ and 5, the (*E*, *E*) isomer is the dominant species. The location of a solvent molecule farther from the ion core makes the *Z* conformation more unstable. In the previous study, it was shown that chain structures terminated by cyclic dimer units at both ends become preferable for larger clusters (see Figs. 4, 5, and 8 of ref. 14).[14] In order to form a cyclic dimer unit at the end of chain structures, the solvent molecules at the periphery should have the *E* conformation. In smaller clusters, the stable *Z* conformation inhibits the chain termination by cyclic dimer units. Figure 3 displays the infrared photodissociation spectra of $H^+•(HCOOH)_{5–7}$ in the free OH region. There is a sharp band of the free OH stretching in the spectra of $n = 5$ and 6; it disappears for the $n = 7$ ion. Therefore, we conclude that both ends of the chain structure are completely terminated by cyclic dimers for $n = 7$.

In the infrared spectrum of the $n = 3$ ion, a broad band is observed in the 3000–3700 cm^{-1} region; the intensity increases with decreasing the frequency. We tentatively assign this absorption to the hydrogen-bonded OH stretching vibrations of the ion core, although the maxima may be located at lower than 3000 cm^{-1}. The calculations predict the hydrogen-bonded OH bands at 2169 and 2425 cm^{-1} for the (*E*, *Z*) isomer, and 2044 and 2683 cm^{-1} for the (*E*, *E*) isomer. The $n = 4$ and 5 ions have one broad band with a maximum at 3220 and 3240 cm^{-1}, respectively. These bands are ascribed to the hydrogen-bonded OH stretching vibration of the molecules at the first solvation shell. Estimated frequencies are 3100 cm^{-1} ($n = 4$), and 2818 and 3183 cm^{-1} ($n = 5$).

B. H^+•$(CH_3COOH)_n$ (n = 2–5)

The infrared photodissociation spectra of H^+•$(CH_3COOH)_n$ (n = 2–5) are shown in Figs. 1e–h. The spectra well resemble those of the formic acid clusters (Figs. 1a–d). The $n = 2$ and 3 ions have two sharp bands; the intensity of the high-frequency band decreases from $n = 2$ to 3. The $n = 4$ and 5 ions have only one sharp band around 3565 cm^{-1}. Band positions are summarized in Table 1. Resemblance of the spectra between the formic acid and acetic acid clusters manifests similar intermolecular configurations; only the COOH group is involved in intermolecular bond formation. This experimental result is consistent with the theoretical one reported by Zhang and Lifshitz.[14] They suggested that the stable structures of the acetic acid clusters could be deduced by replacing H by CH_3 in the optimized structures of the formic acid clusters.

In detail, band positions are slightly different between the formic acid and acetic acid clusters. As seen in Table 1, the band positions of the acetic acid clusters are higher than those of the formic acid clusters by ~ 20 cm^{-1}. It can be understood from the fact that acetic acid has the frequency of the OH stretching vibration (3577 cm^{-1})[xxvi] higher than that of formic acid (3550.5 cm^{-1}).[25] For $n = 4$ and 5, widths of the bands around 3200 cm^{-1} are broader for the acetic acid clusters than for the formic acid ones. This result is originated from difference in the density of states. The density of states of the acetic acid system is higher than that of the formic acid system due to the presence of a methyl group in acetic acid. The higher density of states results in shorter lifetime of the vibrational excited states coupled with intermolecular vibrational modes, giving broader band widths for the acetic acid clusters.

4. Conclusion

The infrared photodissociation spectra of $H^+\bullet(HCOOH)_n$ and $H^+\bullet(CH_3COOH)_n$ (n = 2–5) have been measured. For $H^+\bullet(HCOOH)_n$, the intensity of the free OH stretching band of the *Z* conformation decreases with increasing cluster size from $n = 2$ to 3. This result suggests that the (*E*, *Z*) isomer becomes more unstable than the (*E*, *E*) isomer for larger clusters. The $n = 4$ and 5 ions have only the (*E*, *E*) isomers. The infrared spectrum of $H^+\bullet(HCOOH)_7$ suggests that both ends of the chain structure are terminated by cyclic dimers for $n = 7$. The infrared spectra are quite similar between the formic acid and acetic acid systems; only the COOH group is involved in the intermolecular bonds.

References and notes

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[xxii] When the hydrogen atom of the OH group and the substituent R are on the same side of the C–O single bond, the conformation is designated as *Z*. If these are on opposite sides, the designation is *E*.

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Figure Captions

Figure 1. Infrared photodissociation spectra of $H^+ \bullet (HCOOH)_n$ (a–d) and $H^+ \bullet (CH_3COOH)_n$ (e–h) with $n = 2–5$.

Figure 2. Optimized structures of HCOOH (a) and $H^+ \bullet (HCOOH)_n$ with $n = 1$ (b), 2 (c, d), 3 (e, f), 4 (g), and 5 (h).

Figure 3. Infrared photodissociation spectra of $H^+ \bullet (HCOOH)_n$ with $n = 5–7$ in the free OH stretching region.

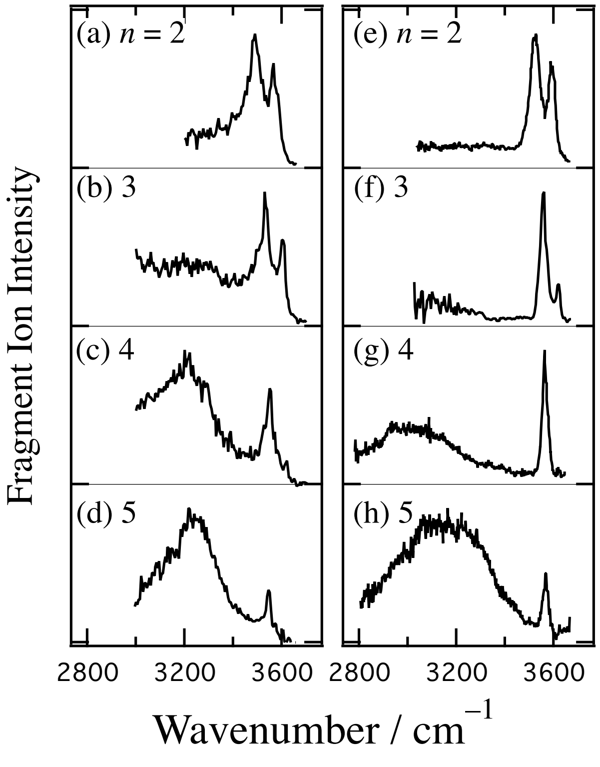
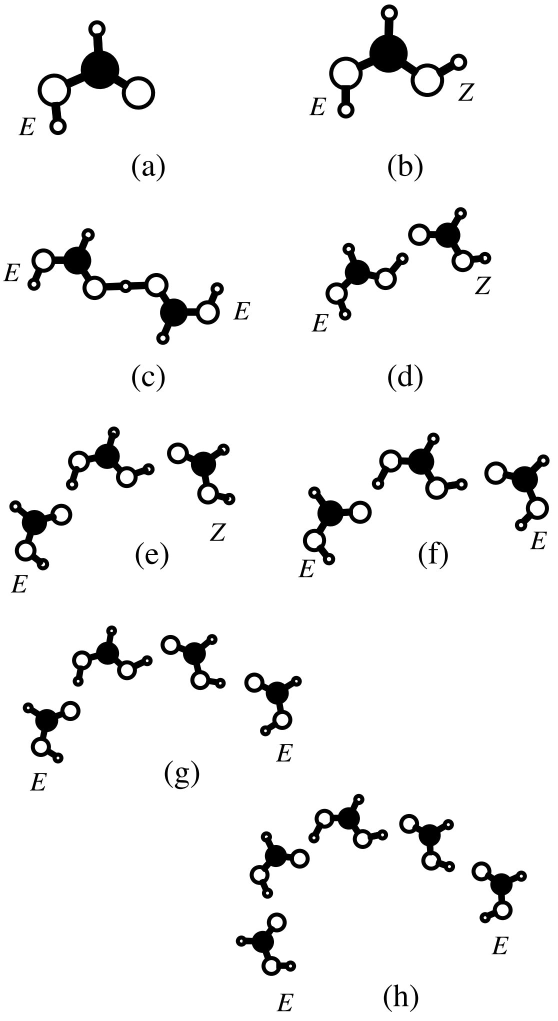


Figure 1. Inokuchi and Nishi



(a) (b) (c) (d) (e) (f) (g) (h)

Figure 2. Inokuchi and Nishi

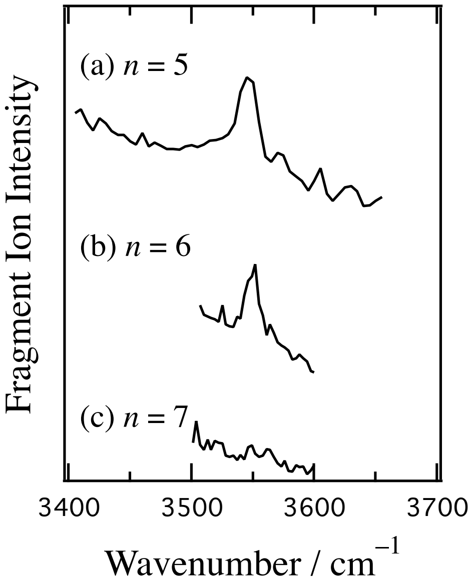


Figure 3. Inokuchi and Nishi

Table 1. Observed band positions (cm^{-1}), calculated band positions[a] (cm^{-1}) and intensities (km/mol, in parentheses), and assignments of the free OH stretching vibrations of $H^+\bullet(RCOOH)_n$ (R = H and CH_3).

n	H	calculated (R = H)	CH_3	Assignment
2	3489	3505 (331),[b] 3506 (0),[b] 3499 (174)[c]	3524	*E*
	3565	3572 (211)[c]	3590	*Z*
3	3532	3529 (115),[c] 3527 (119),[b] 3549 (97)[b]	3557	*E*
	3600	3585 (168)[c]	3617	*Z*
4	3547	3534 (107),[b] 3550 (86)[b]	3564	*E*
5	3545	3541 (93),[b] 3552 (82)[b]	3566	*E*

[a] A scaling factor of 0.9521 is used.

[b] Values of (*E*, *E*) isomers.

[c] Values of (*E*, *Z*) isomers.