Laser Spectroscopic Investigation of Salicylic Acids Hydrogen Bonded with Water in Supersonic Jets: Microsolvation Effects for Excited State Proton Dislocation

Eman Abd El-Hakam Abou El-Nasr, Asuka Fujii,* Toru Yahagi, Takayuki Ebata,† and Naohiko Mikami*

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

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Geometric structures and excited-state proton dislocation of size-selected salicylic acid clusters (salicylic acid and 5-methoxysalicylic acid) with water were studied by using laser spectroscopic techniques. Fluorescence excitation, dispersed fluorescence, and infrared (IR) spectra of those clusters in supersonic jets were examined for both the electronic ground (S_0) and first excited (S_1) states. The geometric structures of the clusters were determined on the basis of the IR spectra of the OH stretch region with the help of quantum chemical calculations. The hydroxyl group of the water moiety in the clusters forms a ring involving the carboxylic group of the salicylic acid moiety. The IR spectra in S_0 show that the intramolecular hydrogen bond in the salicylic acid moiety is still held upon cluster formation, but the phenolic OH stretch band intensity is remarkably weaken in the clusters. The IR spectra in the S_1 state and dispersed fluorescence spectra indicated that the intramolecular excited state proton dislocation is hardly affected by the microsolvation with water, in contrast with the strong suppression of the dislocation in the self-solvation.

I. Introduction

Since the first report by Weller, the largely Stokes shifted emission in salicylic acid (SA) and its derivatives has been attributed to the excited-state intramolecular proton transfer (ESIPT).[1,2] Such molecules have an intramolecular hydrogen bond between the phenolic OH and the neighboring carbonyl oxygen. In the first electronic excited state (S_1), both the acidity of the phenolic OH and the basicity of the carbonyl oxygen are significantly enhanced, and the enhancement of the intramolecular hydrogen bond strength has been a major reason for the idea of ESIPT. The traditional interpretation of ESIPT by Weller involves a double minimum potential associating with the enol−keto tautomerism for the reaction coordinate in S_1.[1,2] Recent studies of SA derivatives, however, supported a single minimum potential for S_1,[3−14] and the large Stokes shift in the emission spectra is attributed to an extensive rearrangement of the whole H-chelate ring, where the excited state H atom displacement along the OH bond is estimated to be only about 0.15−0.32 Å with respect to the equilibrium in the electronic ground state (S_0).[9,10] Therefore, for SA derivatives, a terminology of "excited state proton dislocation" is currently preferred rather than "excited state proton transfer".[9−14]

A competition between intra- and intermolecular hydrogen bonds is an important subject for understanding solvation effects of intramolecularly hydrogen-bonded compounds. Laser spectroscopic investigations of jet-cooled molecular clusters have been carried out to establish a microscopic picture of such a competition.[5,7,8,11−16] Weakening and cleavage of the intramolecular hydrogen bond due to the competing intermolecular hydrogen bond formation have been reported so far.[15,16] With respect to the microsolvation effect of the excited-state proton dislocation in SA, Lahmani and Zehnacker-Rentien investigated the cluster formation of SA with methanol (MeOH), acetic acid, and trifluoroacetic acid.[7] For acetic acid and trifluoroacetic acid, they supposed a cyclic structure where two intermolecular hydrogen bonds are formed between the carboxylic groups. On the basis of fluorescence spectroscopy, Lahmani and Zehnacker-Rentien concluded that the cluster formation with methanol leads to no remarkable effect on the emission property of SA, while the cluster formation with acetic and trifluoroacetic acids strongly suppresses the Stokes shift in the dispersed fluorescence spectra.

The emission property of the SA homodimer was also studied extensively.[5,7,11,17−21] Similar to the heteroclusters with acetic and trifluoroacetic acids, the Stokes shift is remarkably reduced upon the homodimer formation. We applied infrared (IR) spectroscopy to the homodimer, and we confirmed a cyclic structure where two equivalent intermolecular hydrogen bonds are formed between the carboxylic groups.[11] We also found that the intramolecularly hydrogen-bonded phenolic OH stretch is hardly affected by the electronic excitation, and we concluded the strong suppression of the excited-state proton dislocation in the homodimer.[11]

Recently, an amino relative of SA, anthranilic acid, and its clusters were extensively studied by Zwier and co-workers.[13,14,21] Excited-state proton dislocation of the amino hydrogen was confirmed for the monomer, and the magnitude of the proton dislocation was much less than that of SA, reflecting the weaker acidity of the amino group.[13] Structure and excited-state dynamics of the anthranilic acid−water cluster were also studied.[14] A ring structure was determined on the basis of IR spectroscopy and quantum chemical calculations. In this ring structure, the carboxylic OH donates a proton to the water oxygen, and one of the water OH groups also donates a proton to the carbonyl oxygen. Zwier and co-workers also concluded that the cluster formation between anthranilic acid and water

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* To whom correspondence should be addressed. E-mail: asuka@qclhp.chem.tohoku.ac.jp, nmikami@qclhp.chem.tohoku.ac.jp.

† Present address: Department of Chemistry, Graduate School of Science, Hiroshima University, Higashihiroshima 739-8526, Japan.

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exhibits no remarkable effect on the excited-state intramolecular proton dislocation.

In the present work, we investigated structures of SA and 5-methoxysalicylic acid (5-MeOSA) clusters with water. SA is the most fundamental molecule among its relatives which exhibit the excited-state intramolecular proton dislocation, and the methoxy substitution at the 5-position (para to the hydroxyl group) is known to cause a remarkable reduction of the dislocation.[8,12] We applied both the electronic and IR spectroscopy in S_0 and S_1 to these clusters, and the IR spectroscopy especially probed the OH stretching vibrations which are closely related to the hydrogen-bonded structures. Microsolvation effects on the excited-state intramolecular proton dislocation are discussed in comparison with the effect due to the self-solvation upon the homodimer formation.

II. Experimental Section

Details of the experimental setup used in this work can be found elsewhere.[22] Briefly, fluorescence excitation, dispersed fluorescence, IR−UV (IR spectroscopy for S_0), and UV−IR (IR spectroscopy for S_1) spectra of jet-cooled clusters were recorded. The solid sample was heated to 380 K and its vapor was seeded in a helium/water gaseous mixture at the stagnation pressure of 3 atm. The mixture was supersonically expanded through a pulsed nozzle with an orifice 0.8 mm in diameter. The samples were purchased from Tokyo Kasei Co., and were used without further purification.

Fluorescence excitation spectra were recorded by monitoring the laser induced fluorescence while scanning the excitation laser wavelength. The excitation laser light was a second harmonic of a dye laser output (Lumonics HD-500) pumped by a second harmonic of a Nd:YAG laser output (Continuum Surelite-II). The laser induced fluoresce was detected by a photomultiplier tube (Hamamatsu 1P-28) after passing through color filters (Corning 7-59 and Toshiba L-39). Dispersed fluorescence spectra were recorded by using a monochromator (Nikon G-250) with a spectral resolution of 100 cm^{-1}. The signal was processed through a gated integrator boxcar to a personal computer.

IR spectra were observed for S_0 and S_1 by using the IR−UV and UV−IR double resonance techniques, respectively.[21−23] IR−UV spectra for S_0 are recorded by monitoring the fluorescence pumped by a pulsed tunable UV laser, of which the wavelength is tuned at the 0−0 band of the S_1-S_0 transition. The fluorescence intensity represents a measure of the population of the vibrational ground level of S_0. A tunable IR light pulse is introduced prior to the UV pulse by 50 ns. When the IR frequency is resonant with the vibrational transition, a depletion of the fluorescence signal occurs due to the reduction of the population in the vibrational ground level. In UV−IR spectroscopy for S_1, on the other hand, the IR laser pulse is introduced just after the UV laser pulse. The vibrational transition in the S_1 state results in the reduction of the fluorescence when the fluorescence quantum yield of the vibrationally excited level is lower than that of the vibrational ground level. Thus an IR spectrum is obtained as a depletion spectrum by monitoring the fluorescence intensity while scanning the IR frequency. The IR light pulse was generated by difference frequency generation (DFG) between the second harmonics of a Nd:YAG laser (Quanta-Ray GCR/230) and the output of a Nd:YAG laser pumped dye laser (Continuum ND6000, DCM dye) with a $LiNbO_3$ crystal.

III. Results and Discussion

1. Electronic Spectroscopy. Electronic spectroscopy of jet-cooled SA has first been reported by Bisht et al.,[5] and the origin band of the SA monomer was found at 29 811 cm^{-1}. A band at 29 900 cm^{-1} was assigned to a vibronic band of the SA monomer in the first report by Bisht et al., but the present IR−UV spectroscopy reveals that this band must be the origin of the SA−H_2O cluster, as will be described later. On the other hand, the origin band of the S_1-S_0 transition of bare 5-MeOSA appears at 28 151 cm^{-1}.[8,12] In contrast to the clusters of SA, the origin transition of the 5-MeOSA−H_2O cluster is found to be low-frequency shifted by 21 cm^{-1} from the origin of the bare molecule.

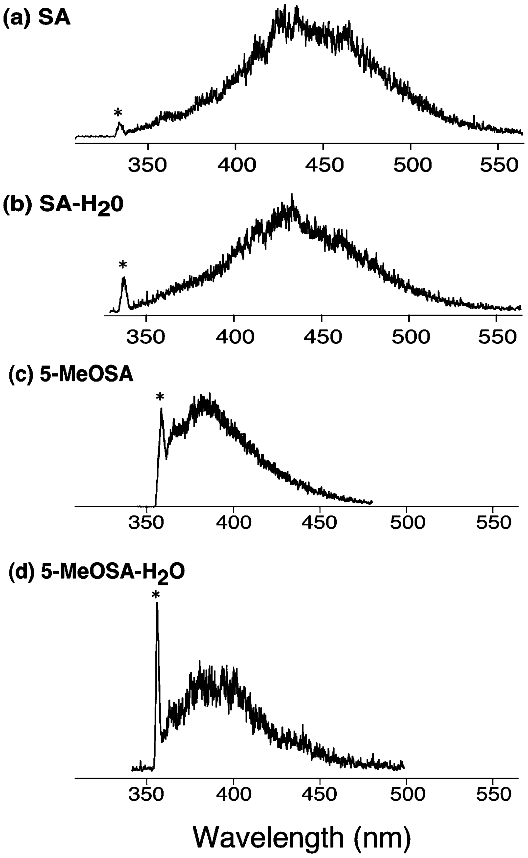

Figure 1. Dispersed fluorescence spectra of (a) bare salicylic acid (SA), (b) SA−H_2O, (c) bare 5-methoxysalicylic acid (5-MeOSA), and (d) 5-MeOSA−H_2O observed by the origin band excitation. The asterisked peaks are due to the scattering light of the excitation laser.

Figure 1 shows the dispersed fluorescence spectra of jet-cooled (a) bare SA, (b) SA−H_2O, (c) bare 5-MeOSA, and (d) 5-MeOSA−H_2O obtained by exciting their origin bands. The dispersed fluorescence spectra of the jet-cooled SA and 5-MeOSA monomers have been reported by Bisht et al.[5] and by Lahmani and Zehnacker-Rentien,[8] respectively. A large Stokes shift with a maximum at 430 nm is seen in the spectrum of the SA monomer. Such a large Stokes shift is known as a characteristic feature of the excited-state proton dislocation. The Stokes shift of the 5-MeOSA monomer is clearly reduced in comparison with that of SA. This is a substitution effect of the methoxy group in the para position with respect to the phenolic OH, and the noticeable suppression of the excited-state proton dislocation is evident.[8,12] Both the spectra of the water clusters are similar to those of the corresponding bare molecules. It suggests that the microsolvation with water makes no substantial change in the magnitude of the proton dislocation of the bare molecules. A similar result was reported for SA-MeOH by Lahmani and Zehnacker-Rentien.[7]

2. Infrared Spectroscopy. *a. OH Stretching Vibrations in S_0.* Figure 2 shows the OH stretching vibrational region of the

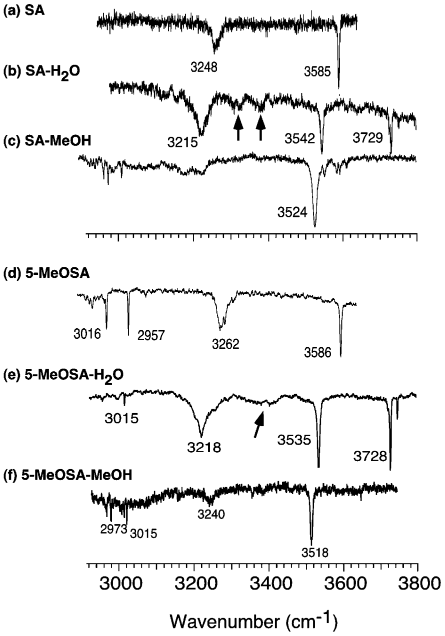

Figure 2. Infrared (IR) spectra of (a) SA, (b) SA−H_2O, (c) SA−methanol, (d) 5-MeOSA, (e) 5-MeOSA−H_2O, and (f) 5-MeOSA−methanol in the electronic ground (S_0) state. The IR−UV double resonance technique was utilized to measure the IR spectra in S_0. Arrows indicate the candidate bands for the phenolic OH stretch band in the clusters (see text).

IR spectra in S_0 of jet-cooled (a) bare SA, (b) SA−H_2O, (c) SA−MeOH, (d) bare 5-MeOSA, (e) 5-MeOSA−H_2O, and (f) 5-MeOSA−MeOH. The IR spectra of the methanol clusters were measured for comparison with the spectra of the water clusters, as described later. The spectra of the SA and 5-MeOSA monomers have been analyzed in our previous papers.[11,12] Both of the monomers show a very similar spectral feature; the sharp band around 3585 cm^{-1} is attributed to the free OH stretch of the carboxylic group, and the relatively broad band around 3250 cm^{-1} is assigned to the phenolic OH stretch, which is intramolecularly hydrogen bonded to the carbonyl oxygen. Sharp bands around 3000 cm^{-1} in the spectrum of 5-MeOSA are attributed to the CH stretches of the methoxy group.

In the IR spectrum of SA−H_2O, though four OH stretch bands are expected to appear, only three clear bands are seen in the 3 μm region. Two sharp bands appear at 3729 and 3542 cm^{-1}, and one broad and intense feature is found at 3215 cm^{-1}. The sharp band at 3729 cm^{-1} is unambiguously attributed to the free (dangling) OH stretch of the water site, which is often seen in water-containing small clusters.[14−16,22−24] The position of the band at 3542 cm^{-1} is clearly lower than the free carboxylic OH stretch of the monomer (3585 cm^{-1}), and it is also too high for a hydrogen-bonded carboxylic OH stretch. Then, it is reasonably assigned to another OH stretch of the water moiety, which is hydrogen bonded to the SA site. The broad band at 3215 cm^{-1} seems to be very similar to the phenolic OH band of the monomer with respect to the band position and width, and it might be naively assigned to the phenolic OH stretch. However, an alternative assignment, the carboxylic OH stretch being strongly hydrogen bonded to the water site, is also probable because the free carboxylic OH band disappears in the spectrum of the cluster. It is clear that one of these two candidates is missing in the observed IR spectrum, demonstrating that the intensity reduction or large shift over the observed range occurs upon the cluster formation.

The IR spectrum of 5-MeOSA−H_2O is very similar to that of SA−H_2O, in contrast with remarkably different features of the dispersed fluorescence spectra shown in Figure 1. Frequency shifts of the OH stretches due to the methoxy substitution are not remarkable, and it suggests that the quite different emission property of 5-MeOSA from that of SA is attributed to differences in the S_1 state. The similar assignments as those of SA−H_2O can be made for the IR spectrum of 5-MeOSA−H_2O;. the free and hydrogen-bonded OH stretches of the water moiety are seen at 3728 and 3535 cm^{-1}, respectively, and a weak band at the high-frequency side of the free water OH would be a combination band between the water OH stretch and an intermolecular vibration, as is often seen in hydrated clusters. The relatively broad absorption at 3218 cm^{-1} is attributed to the phenolic or carboxylic OH stretch, and one of these two candidates seems to be missing, as the same puzzling feature is seen in the SA cluster.

To obtain more information for the assignment of the broad band around 3200 cm^{-1} of the water clusters, we also observed the IR spectra of SA-MeOH and 5-MeOSA−MeOH, as shown in Figure 2, parts c and f. The S_1−S_0 origin band of SA−MeOH appears at 29 880 cm^{-1}, being high frequency shifted by 69 cm^{-1} with respect to the origin of the SA monomer.[7] The origin transition of the 5-MeOSA−MeOH cluster is found at 28 128 cm^{-1}. This is low-frequency shifted from the origin of the monomer.[8] The IR spectra of the methanol clusters exhibit similar features to those of the water clusters, except for the reasonable absence of the free OH band. In SA−MeOH, a sharp and intense band appears at 3524 cm^{-1} and a weak broad absorption is seen around 3200 cm^{-1}. The former band is clearly attributed to the hydrogen-bonded OH stretch of the methanol moiety, and the later would correspond to the 3215 cm^{-1} band of SA−H_2O, but the band is much broader and weaker. Potential candidates for this band are the phenolic and carboxylic OH stretches, the same as the case for SA−H_2O, and one OH stretch band disappears also in the spectrum of SA−MeOH. Weak and sharp peaks around 3000 cm^{-1} are attributed to the CH stretches of the methanol moiety. The spectrum of SA−MeOH is essentially the same as that of SA−H_2O, and it is unexpectedly not helpful for the assignment of the broad band at 3200 cm^{-1}.

In every IR spectrum of the clusters, the carboxylic OH is no longer seen in the free OH region, and it indicates that the carboxylic OH forms a hydrogen bond in the clusters. In addition, one hydrogen-bonded OH band of the water (or methanol) moiety appears in the spectra of the clusters. These facts strongly suggest that the cluster structure should be a ring form, where the water (methanol) OH bridges the carboxylic OH and carbonyl oxygen, though the assignment of the broad band around 3200 cm^{-1} in the cluster spectra is not uniquely determined in this qualitative discussion. Then, to confirm the cluster structure and band assignments, energy optimized structures and corresponding simulated IR spectra of the clusters were calculated at the B3LYP/6-31+G* level. Zwier and coworkers have demonstrated that this level of density functional theory (DFT) calculations is successful to reproduce the observed IR spectra of the anthranilic acid−water cluster.[13,14,21] The computation was carried out by using the Gaussian 03 program package.[26] Figures 3 and 4 show the energy optimized structures and comparisons between the observed IR spectra and simulated IR spectra corresponding to the optimized structures.[27]

As was already discussed in our previous paper,[11] the observed IR spectrum of the SA monomer is well reproduced by the simulated spectrum of the rotamer where the phenolic OH is intramolecularly hydrogen bonded to the neighboring

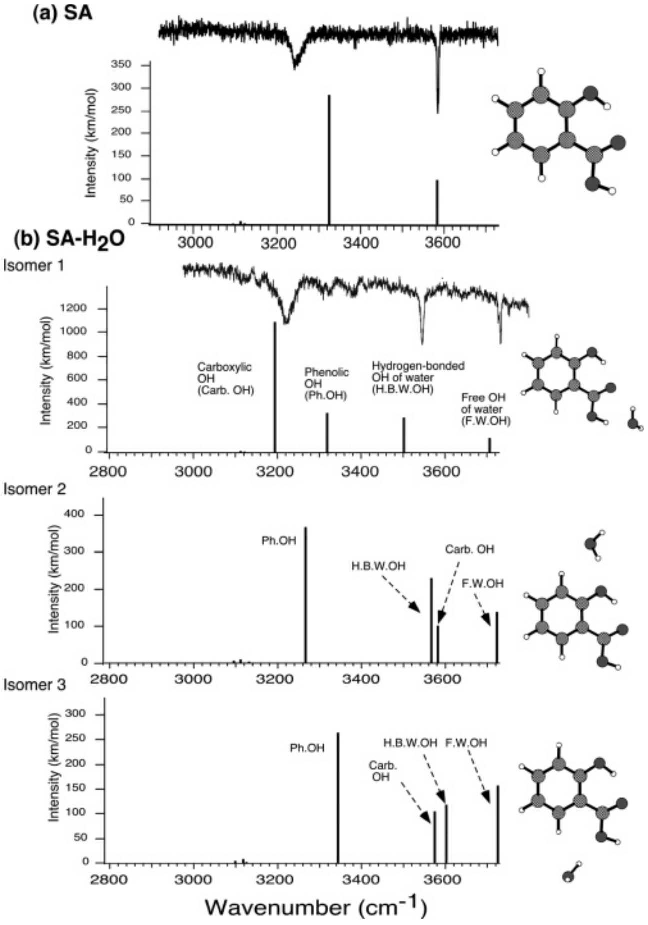

Figure 3. Comparison between the observed and simulated IR spectra of (a) SA and (b) SA$-$H$_2$O in S$_0$. Each simulated IR spectrum was calculated on the basis of the energy optimized structure schematically shown in the inset. The calculation level was B3LYP/6-31+G*, and a scaling factor of 0.9704 was applied to all the calculated harmonic frequencies (see text).

carbonyl oxygen. Figure 3a shows the comparison between the observed and simulated IR spectra of the SA monomer.

Three isomer structures were found for SA$-$H$_2$O, which are shown in the insets of Figure 3b. The most stable isomer (isomer **1**) has the ring type structure, where the water molecule acts as a proton acceptor as well as a proton donor and makes a bridge between the carboxylic OH and the carbonyl oxygen. Two other isomers have a single intermolecular hydrogen bond, in which the water molecule donates the proton to the phenolic OH (isomer **2**) or to the carboxylic OH (isomer **3**) of SA. Isomers **2** and **3** are estimated to be less stable than isomer **1** by +5.39 and +7.38 kcal/mol, respectively, including the zero point energy (ZPE) corrections. Simulated IR spectra of these isomer structures are compared with the observed spectrum in Figure 3b. A scaling factor of 0.9704 was applied for all the calculated harmonic frequencies. This factor was determined to fit the calculated free carboxylic OH stretch frequency of the monomer to the observed one. The simulated IR spectrum of isomer **1** shows the best overall agreement with the observed one. Further improvement of the spectral simulation would be expected if the scaling factor is determined to optimize the simulation of isomer **1**. This spectral simulation based on isomer **1** strongly suggests that the broad band at 3215 cm^{-1} in the observed spectrum is assigned to the hydrogen-bonded carboxylic OH stretch. Though the simulation predicts the phenolic OH stretch at around 3320 cm^{-1} with almost the same intensity as that of the monomer, the observed IR spectrum in this region shows only extremely weak and broad bumps indicated by arrows in Figure 2b. These weak absorptions appearing at around 3320 and 3380 cm^{-1} are tentatively assigned to the band due to the phenolic OH stretch. On the other hand, in both isomers **2** and **3**, two bands due to the free carboxylic OH and hydrogen-bonded OH of the water moiety are expected to appear around 3600 cm^{-1}. The observed spectrum clearly shows a single OH band in this region, and such a discrepancy cannot be reasonably explained. Therefore, both the stabilization energy and IR spectral simulation support the ring structure (isomer **1**) for the observed SA$-$H$_2$O cluster, and this is consistent with the qualitative discussion on the basis of the observed IR spectrum.

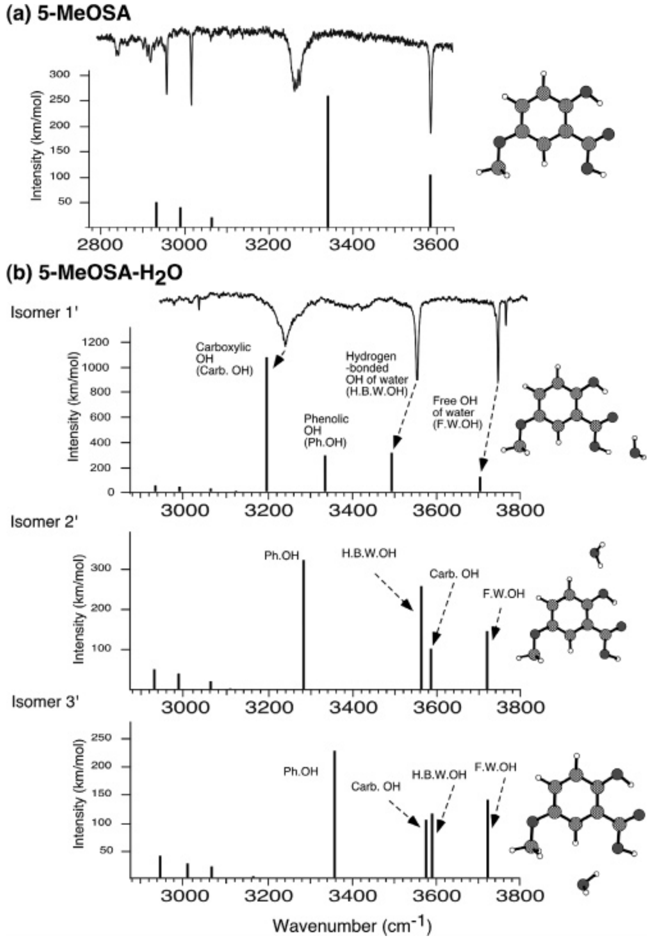

Figure 4. Comparison between the observed and simulated IR spectra of (a) 5-MeOSA and (b) 5-MeOSA$-$H$_2$O in S$_0$. Each simulated IR spectrum was calculated on the basis of the energy optimized structure schematically shown in the inset. The calculation level was B3LYP/6-31+G*, and a scaling factor of 0.9704 was applied to all the calculated harmonic frequencies (see text).

All the structural optimizations, which started from initial structures having interactions between the water molecule and the phenolic OH or carboxyl group, finally converged to one of the isomers **1**$-$**3**. Structural isomers other than isomers **1**$-$**3**, such as π-hydrogen-bonded and CH$-$O hydrogen-bonded isomers, would be present as local minima of SA$-$H$_2$O, though we did not survey such isomers in the present calculations. However, they cannot be attributed to the observed IR spectrum because it is clear that such interactions are much weaker than the hydrogen bonds between the water molecule and the carboxyl group.

Bare 5-MeOSA has several rotamers with respect to the methoxy group conformations. The lowest energy rotamer in the calculations is shown in an inset of Figure 4a. The observed

IR spectrum of the monomer is well-reproduced by the simulation based on this rotamer. Two more rotamers were found in the calculations. They show essentially the same IR spectrum in the OH stretch region, and the energy differences among the rotamers are also very small (0.91−2.27 kcal/mol). Because the methoxy conformation would have no essential effect to the microsolvation, we assumed the conformation of the methoxy group to be the most feasible one as shown in the inset of Figure 4a, and used it for the estimation of the cluster structures of 5-MeOSA−H_2O.

Three isomers were found also in the energy optimization of 5-MeOSA−H_2O, as seen in Figure 4b. The isomer structures are very similar to those of SA−H_2O. The ring structure (isomer **1′**) is the most stable, and single intermolecular hydrogen bond structures (isomer **2′** and **3′**) are higher in energy by + 5.34 and +6.71 kcal/mol, respectively. The simulated IR spectra are also very similar to those of SA−H_2O, and the same discussion can be applied to 5-MeOSA−H_2O. The ring structure (isomer **1′**) is strongly supported also for 5-MeOSA−H_2O.

Also in 5-MeOSA−H_2O, the broad band at 3218 cm^{-1} is attributed to the carboxylic OH stretch, on the basis of the spectral simulation. An extremely broad and weak absorption is seen around 3400 cm^{-1}, as indicated by an arrow in Figure 2e, and this absorption is a potential candidate of the "missing" phenolic OH stretch. In the ring cluster formation, the carbonyl oxygen is shared by the water and phenolic OHs. With respect to this point, the high frequency shift of the phenolic OH (reduction of the intramolecular hydrogen bond strength) is expected for the ring cluster, and it is consistent with this assignment. However, no such high frequency shift and intensity reduction of the phenolic OH are actually predicted for the water cluster by the DFT calculation. In addition, overtones of OH bending modes are also often seen in this region. The assignments of the weak bands are not unequivocal at the present stage.

The normal-mode analysis of the simulated spectrum shows that the three hydrogen-bonded OH stretches in the cluster, i.e., carboxylic, phenolic, and water OHs, are almost isolated from each other. Then, it denies the intensity reduction of the phenolic OH due to the mode mixing, which causes cancellation of the transition intensities. The "missing" of the phenolic OH would be attributed to extreme broadening upon the cluster formation, though its mechanism is unclear at present. An alternative explanation might be an accidental overlap between the carboxylic OH and phenolic OH in the broad and intense band. Such an accidental overlap, however, is unlikely for the following reasons: (i) the bands at 3215 and 3218 cm^{-1} in SA−H_2O and 5-MeOSA−H_2O, respectively, exhibit no clear sign of the band overlap, (ii) it requests the low-frequency shift of the phenolic OH upon the cluster formation, which is inconsistent with the ring structure, where the high-frequency shift of the phenolic OH is reasonably expected, and (iii) the DFT calculations also predicted the frequency difference of over 100 cm^{-1} between the carboxylic and phenolic OH bands.

A similar ring type structure has been known for a cluster of an amino relative of SA, anthranilic acid, with water.[14] In the case of anthranilic acid−H_2O, the intramolecularly hydrogen-bonded amino NH stretch clearly appears in the water cluster, and no significant intensity reduction or band broadening was observed upon the water cluster formation. The B3LYP/6-31+G* level calculation successfully reproduced the observed IR feature. Though the origin of the different behavior of the phenolic OH and amino NH upon the cluster formation is not clear, the ring structure for the anthranilic acid−water cluster is a strong support for that for SA−H_2O.

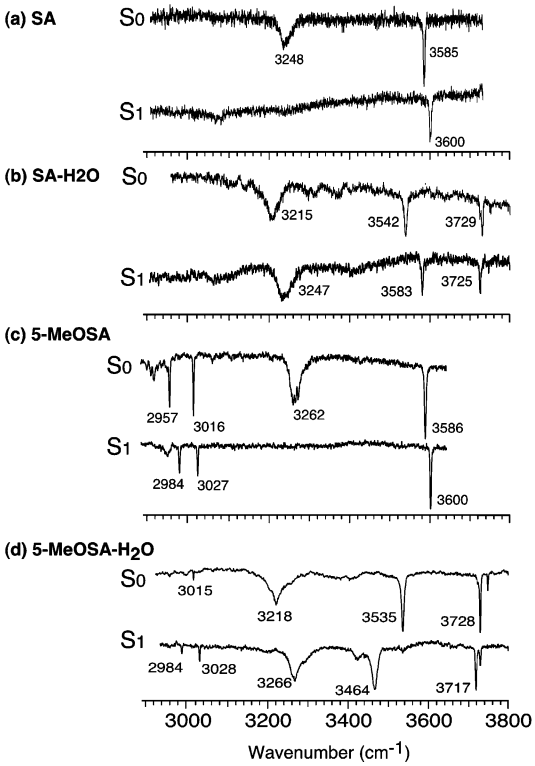

Figure 5. Infrared (IR) spectra of (a) bare SA, (b) SA−H_2O, (c) bare 5-MeOSA, and (d) 5-MeOSA−H_2O in the electronic excited (S_1) state. The spectra in S_0 are also reproduced for comparison. The UV−IR double resonance technique was utilized to measure the IR spectra in S_1, and the origin band was used to excite the vibrational ground level of the S_1 state.

b. OH Stretching Vibrations in S_1. Figure 5 shows the IR spectra in the S_1 state for (a) bare SA, (b) SA−H_2O, (c) bare 5-MeOSA, and (d) 5-MeOSA−H_2O, respectively, and those in S_0 are also reproduced for comparison. Each IR spectrum of S_1 was obtained by pumping the zero vibrational level of the S_1 state. The IR spectra of the monomers in S_1 have been extensively discussed in our previous papers, showing that the phenolic OH band disappears in S_1, while the free carboxylic OH stretch is clearly seen with a small frequency shift.[11,12] The disappearance of the phenolic OH upon electronic excitation is interpreted in terms of the extremely large low-frequency shift to the region below 2900 cm^{-1}. Even for 5-MeOSA, of which the dispersed fluorescence spectrum shows a clear indication of the suppression of the Stokes shift, the phenolic OH band in S_1 disappears from the 3 μm region, demonstrating that the excited-state proton dislocation also does occur, though the deformation of the whole H-chelate ring, which is sensitively reflected in the dispersed fluorescence spectrum, is much less in 5-MeOSA than that in SA.[8,12]

In contrast to the drastic change of the IR spectrum of the SA monomer upon the electronic excitation, the IR spectra of SA−H_2O in S_0 and S_1 seem to be very similar to each other. In the S_1 spectrum, Figure 5b, three OH stretch bands are clearly seen. The sharp bands at 3725 and 3583 cm^{-1} are uniquely assigned to the free and hydrogen-bonded OH stretches of the water moiety, respectively. A broad and intense band at 3247 cm^{-1} is attributed to the hydrogen-bonded carboxylic OH stretch, in comparison with the S_0 spectrum. This is an indirect support for the assignment of the corresponding band in S_0 (3215 cm^{-1}). In the previous section, this assignment was given on the basis of the DFT calculations. If the band at 3215 cm^{-1} in S_0 is assigned to the phenolic OH on the basis of the closely similar feature to the band in the monomer spectrum, the naive assignment of the 3247 cm^{-1} band in the S_1 spectrum would also be the phenolic OH. This assignment means the very small shift of the phenolic OH upon the electronic excitation, and it leads to the conclusion that the proton dislocation of the cluster is completely prohibited in S_1. However, the dispersed fluorescence spectrum of SA$-$H$_2$O shows a substantial Stokes shift which is as large as that in the monomer, as seen in Figure 1. Such a shift has been interpreted as an indication of the extensive deformation of the whole H-chelate ring.[9,10] Because the deformation of the whole H-chelate ring should be associated with the elongation of the phenolic OH bond that results in the remarkable low-frequency shift of the OH stretch, this assignment of the S_1 IR spectrum totally conflicts with the conventional interpretation of the Stokes shifts in dispersed fluorescence spectra of SA derivatives. With respect to this point, it is strongly supported that the 3247 cm^{-1} band in the S_1 IR spectrum should be attributed to the carboxylic OH stretch.

The IR spectrum of 5-MeOSA$-$H$_2$O in S_1 is also similar to that of SA$-$H$_2$O, and it is clear that the same band assignments as those of SA$-$H$_2$O can also be applied. The free and hydrogen-bonded OH stretches of the water moiety appear at 3717 and 3464 cm^{-1}, respectively, in S_1. A broad band is seen at 3266 cm^{-1}, and this band is assigned to the carboxylic OH band, which appears at 3218 cm^{-1} in S_0. Sharp and weak bands around 3000 cm^{-1} are CH stretches of the methoxy group.

In both SA$-$H$_2$O and 5-MeOSA$-$H$_2$O, the frequency shifts of the carboxylic and water OH bands upon the electronic excitation are quite small, and this is a clear indication that the ring structure of the cluster is held in S_1. Despite the sharp contrast between the dispersed fluorescence spectra of SA$-$H$_2$O and 5-MeOSA$-$H$_2$O, the IR spectra of both species are very similar with each other even in S_1. The similarity suggests that the geometrical changes reflected in the dispersed fluorescence would be localized in the H-chelate ring of the phenolic OH and carbonyl groups for both the species. The phenolic OH stretch should be the most sensitive indicator of such a deformation of the H-chelate ring. Because the phenolic OH is almost “missing” even in S_0 of the clusters, the band assignment in S_1 is more difficult. However, no clear band that can be attributed to the phenolic OH is seen in the S_1 IR spectra of both clusters, and it is most reasonable that the phenolic OH of the clusters is also completely missing because of the large low-frequency shifts beyond the observed range, the same as those of the monomers. This is consistent with the similarity of the dispersed fluorescence spectra between the cluster and monomer. Though unassigned small bumps are seen in the S_1 IR spectra of the cluster, for example, at 3420 cm^{-1} in the S_1 spectrum of 5-MeOSA$-$H$_2$O, such a high-frequency shift of the phenolic OH upon electronic excitation is hard to accept with respect to the consistency with the dispersed fluorescence spectra and the monomer IR spectra. Therefore, we conclude that the phenolic OH of the water clusters of SA and 5-MeOSA disappears from the 3 μm region upon electronic excitation, similar to those of the monomers.

The present electronic and IR spectroscopic study demonstrated that the microsolvation with water exhibits a minor effect on the excited-state proton dislocation of SA and 5-MeOSA. Lahmani and Zehnacker-Rentien suggested similar phenomenon for these molecules on the basis of the dispersed fluorescence spectroscopy.[7,8] The present study demonstrates much more detailed evidence on the proton dislocation in S_1 with the direct observation of the OH stretching vibrations. IR spectroscopy of S_1 was applied to anthranilic acid$-$H$_2$O by Zwier and co-workers,[14] and they also concluded the minor effect of the cluster formation, though the key vibration, i.e., the intramoleculary hydrogen-bonded amino NH, was not observed in the S_1 state as in the case of this cluster. In comparison with the straightforward IR spectra of anthranilic acid$-$H$_2$O, those of SA$-$H$_2$O and 5-MeOSA$-$H$_2$O are more puzzling, requiring much detailed discussion for the assignments of the spectra.

The minor effect of the microsolvation of SA with water exhibits a sharp contrast to the self-solvation, i.e., the formation of the SA homodimer, where the remarkable suppression of the proton dislocation was confirmed in both the electronic and IR spectroscopy.[11] The solvation of the carbonyl oxygen would be the key to untangle the complexity about the difference between the SA$-$water cluster and the homodimer. In both cases, the cluster structures are cyclic, and the carbonyl oxygen accepts two protons. Thus, the intramolecular and intermolecular hydrogen bonds compete with each other. The acidity of the water OH is much weaker than that of the phenolic OH of SA in S_1, and the solvation is almost negligible for the phenolic OH. In the case of the self-solvation, however, the carboxylic OH competes with the phenolic OH under a strong attraction of the nonbonding electrons of the carbonyl oxygen. The strong intermolecular hydrogen bond sacrifices the strength of the intramolecular hydrogen bond, and it strongly suppresses the enhancement of the intramolecular hydrogen bond upon electronic excitation, i.e., proton dislocation. This idea is supported by the dispersed fluorescence study of solvated SA by Lahmani and Zehnacker-Rentien.[7] They observed the dispersed fluorescence of the SA$-$MeOH, $-$acetic acid, and $-$trifluoroacetic acid clusters as well as the SA homodimer, and they found that the Stokes shift is suppressed with the increase of the acidity of the solvents.

IV. Summary

The main purpose of the present work was to investigate the excited-state proton dislocation in jet-cooled water clusters of SA and 5-MeOSA, using both the electronic and IR spectroscopies. In combination with the quantum chemical calculations, the cluster structures were determined to be the ring type, where the water molecule bridges the carboxylic OH and carbonyl oxygen of the SA moiety, and the intramolecular hydrogen bond is found to be preserved upon the cluster formation. The IR spectra in S_1 and dispersed fluorescence spectra of the water clusters demonstrated that the microsolvation with water does not remarkably affect the excited-state proton dislocation, in contrast to the significant suppression of the proton dislocation in the homodimers. Such a difference was explained in terms of the competition between the intra- and intermolecular hydrogen bonds to the carbonyl oxygen.

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