1P047 Ultraviolet and Infrared Laser Spectroscopic Study on Excited State Proton Dislocation in Microsolvated Salicylic Acids

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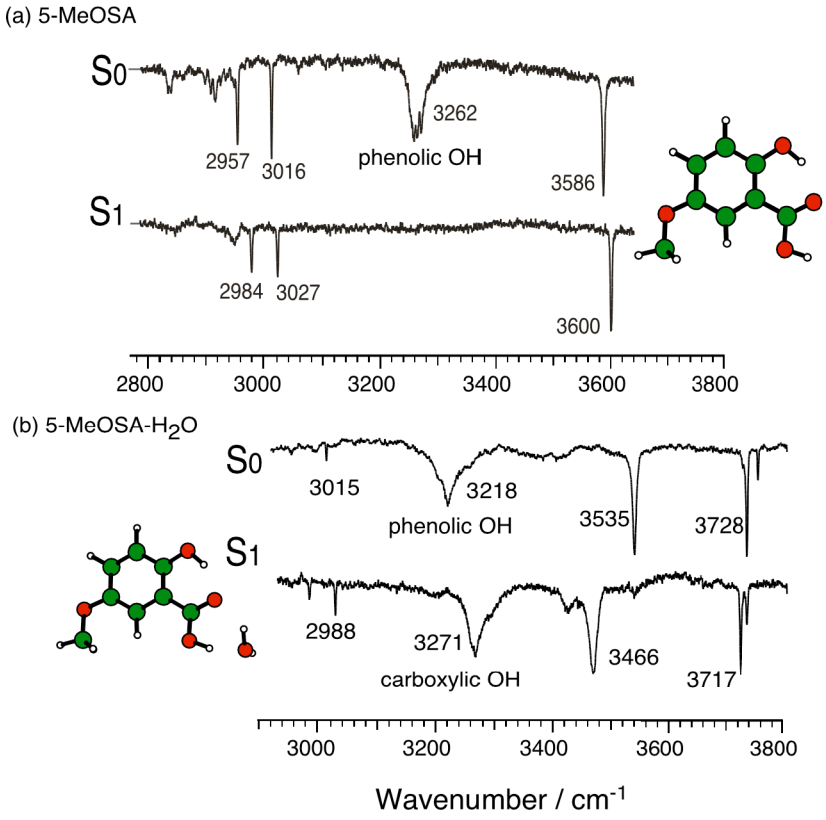
Excited state proton dislocation in size-selected clusters of salicylic acid (SA) and 5-methoxysalicylic acid (5-MeOSA) with water and methanol was investigated by using laser spectroscopic techniques. The geometric structures of the clusters were determined on the basis of the infrared (IR) spectra of the OH stretch region in combination with the quantum chemical calculations. The hydroxyl group of the water or methanol moiety in the clusters forms a ring with the carboxylic group of the salicylic acid moiety. Electronic spectra and IR spectra in both the electronic ground (S_0) and first excited (S_1) states were measured.

The IR spectra of bare 5-MeOSA both in S_0 and S_1 states are presented in Figure 1(a). While the phenolic and carboxylic OH stretching bands appear at 3262 and 3586 cm^{-1}, respectively, in the S_0 spectrum, the phenolic OH band disappears from the 3 μm region in the S_1 spectrum. This phenomenon was explained as a result of the excited state proton dislocation in bare 5-MeOSA. The IR spectra of 5-MeOSA-water cluster are presented in Figure1(b). The S_0 spectrum shows the two OH stretching bands of the water site at 3728 and 3535 cm^{-1} and the phenolic OH band at 3218 cm^{-1}, while no carboxylic OH band is found in this region. This spectrum suggests that it might be shifted to the much lower frequency region due to the strong hydrogen bond formation.

In order to obtain the firm assignments of these bands in the S_1 spectrum, we have carried out a partial deuteration study. We found that the phenolic OH stretching band is still not observed in the 3 μm region while the carboxylic OH band appears at 3271 cm^{-1} due to a

remarkable blue shift upon electronic excitation. Similar spectral feature was observed in other salicylic acid clusters. These observations indicated that the intramolecular excited state proton dislocation is hardly affected by the microsolvation with water or methanol, in contrast to the significant suppression of the proton dislocation in the homodimers.[1] Such a difference can be explained in terms of the competition between the intra- and intermolecular hydrogen bond to the carbonyl oxygen. The present IR spectroscopic results also demonstrated that a drastic reduction of the acidity of the carboxylic OH does occur upon the electronic excitation.

Fig.1:- IR spectra of (a) bare 5-MeOSA and (b) 5-MeOSA-H_2O cluster in S_0 and S_1



[1] T. Yahagi, A. Fujii, T. Ebata, N. Mikami J. Phys. Chem. A, 105 (2001) 10673.