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Substitution effect on the excited state intramolecular proton transfer in jet- cooled salicylic acid studied by infrared spectroscopy

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Introduction:-

Salicylic acid (SA) and its derivatives are well-known molecules having an intramolecular hydrogen bond. The excited-state intramolecular proton transfer (ESIPT) in these molecules has been a subject in a number of studies for many years. Most of experimental information about the substitution effect on ESIPT has been obtained with electronic spectroscopy. In the present work, we investigate the substitution effect from a view point of infrared spectroscopy. We observe the intramolecular and intermolecular hydrogen-bonded OH stretching vibration of various substituted SA in a supersonic jet, for both the electronic ground (S_0) and the first excited state (S_1). Substitution effects are discussed in relation to ESIPT of non-substituted SA[1].

Experiment:-

IR spectra of the jet cooled samples in the S_0 and S_1 states were measured by IR-UV and UV-IR double resonance spectroscopy, respectively [1].

Results and Discussion:-

As seen in Figure 1(a), the electronic emission spectrum of SA exhibits a large Stokes-shift, and it has been regarded as evidence of ESIPT. On the other hand, the emission spectrum of 5-methoxysalicylic acid (5-MeOSA), which is shown in Figure 1(b), does not show a remarkable Stokes-shift, but it exhibits a rather regular feature showing a mirror-image relation with the excitation spectrum. On the basis of such an emission property, the suppression of ESIPT has been suggested for 5-MeOSA[2]. Figure 2 shows the IR spectra of SA and 5-MeOSA in S_0 and S_1.Despite of the above expectation suggested from the electronic spectroscopy, we found that the phenolic OH stretch band of 5-MeOSA shows the similar drastic change as SA upon photoexcitation. In S_0, the phenolic OH band is seen around 3250 cm^{-1}, while the phenolic OH band disappears from the 3μm region in the S_1 state. The disappearance of the OH band is interpreted in terms of the significant low-frequency shift associated with the elongation of the phenolic OH bond, and the magnitude of the elongation is estimated to be larger than 0.1Å.Therefor the IR spectra clearly demonstrate that the remarkable enhancement of the intramolecular hydrogen bond does occur upon photoexcitation of 5-MeOSA[3]. Substitution effects of other substituents are also discussed.

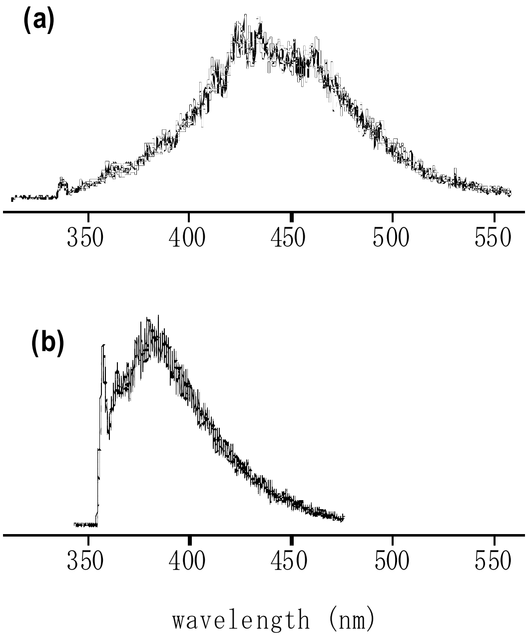

Figure 1 Dispersed fluorescence spectra of (a) SA and (b) 5-MeOSA obtained by excitation of the origin bands of the S_1 - S_0 transition.

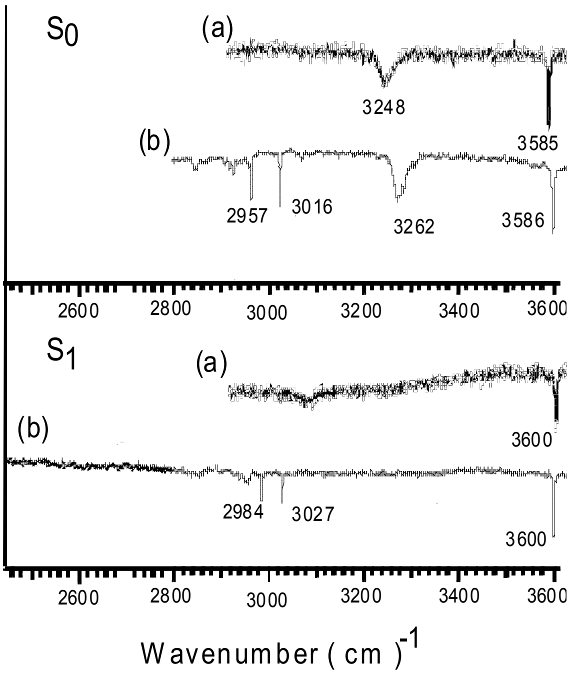

Figure 2 OH stretching vibrational region of the IR spectra in (upper) S_0 and (lower) S_1 of

(a) SA and (b) 5-MeOSA.

References:-

[1] T. Yahagi, A. Fujii, T. Ebata, N. Mikami J. Phys. Chem. A, 105 (2001) 10673.
[2] F. Lahmani, A. Zehnacker-Rentien, J. Phys. Chem. A 101 (1997) 6141.
[3] E. Abou El-Nasr, A. Fujii, T. Ebata, N. Mikami. Chem. Phys. Lett. in press.