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The spectroscopic study of estrogen and its hydrogen bonding abilities

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Introduction: Estrogen(estrone(E_1), β-estradiol(E_2), estriol(E_3)) is an important hormone for human. Estrogen exerts several physiological activities by binding with the estrogen-receptor(ER). In this ligand-receptor interaction, the key points are the hydrogen bonds of phenolic and alcoholic OH with ER. In present study, we investigate the structure of bare estrogen and its hydrated clusters formed in the supersonic jet. Based on the spectroscopic data and quantum chemical calculation, we will discuss their hydrogen(H)-bonding abilities.

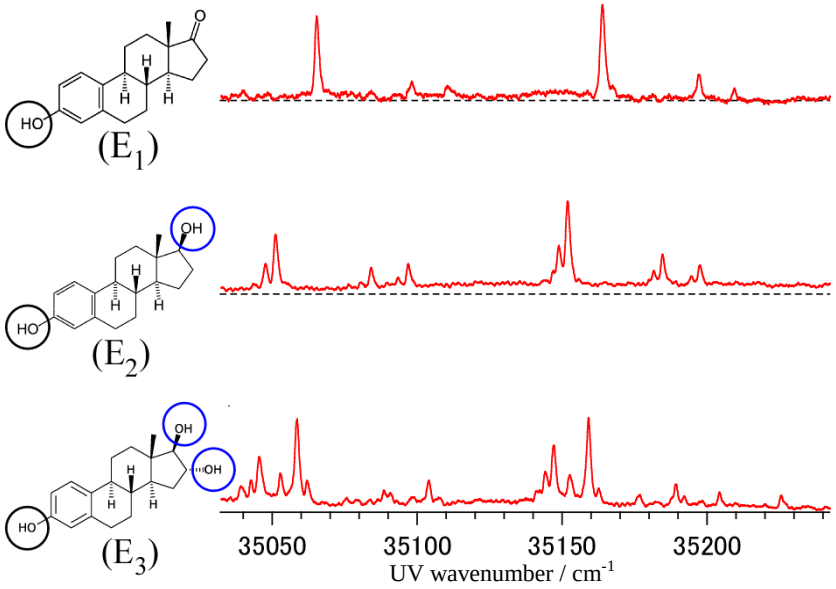

Fig.1 Schematic structures and S_1-S_0 LIF spectra of estrogen monomer. Where, black circles represent phenolic OH and blue are alcoholic.

Experimental and computational: Jet-cooled estrogen and its hydrated clusters are generated by a free jet expansion of gaseous mixture of sample and He carrier gas (and water vapor) in a vacuum chamber. S_1-S_0 electronic spectra were obtained by laser induced fluorescence (LIF). To discriminate vibronic bands belonging to different species in the jet, UV-UV hole burning(HB) spectroscopy was applied. Infrared(IR) spectra were measured by IR-UV double resonance(DR) spectroscopy. Quantum chemical calculations were performed to obtain the stable structures and to analyze the vibrational spectra.

Results and discussion: Fig.1 shows the S_1-S_0 LIF spectra of three estrogen molecules. All spectra exhibit several prominent bands in 35050-35200 cm^{-1}. By measuring the UV-UV HB and IR spectra(not shown here), we conclude they are due to 2 conformers for E_1, 4 conformers for E_2, 6 conformers for E_3, arising from different orientation of the OH group(s). In addition, we found E_3 has an intramolecular H-bond between two alcoholic OH groups in the five-membered ring. Fig.2 shows IR spectra in the OH stretching vibration region of one of the isomers of bare E_2 (a), and E_2-H_2O cluster forming the H-bond at the phenolic OH (b). Also shown is the calculated IR spectrum E_2-H_2O (c). We see that the band at 3658 cm^{-1} of bare E_2 shifts to 3527 cm^{-1} by forming H-bond. From this result, we conclude phenolic OH of E_2 prefers to form the H-bond as a proton acceptor. In the presentation, we also discuss other conformers of estrogen and the relationship between the H-bonding abilities of OH group(s) and ligand-ER binding affinity.

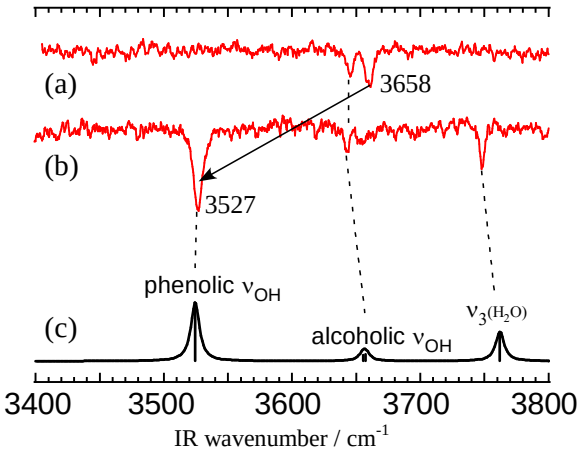

Fig.2 IR spectra of one of (a) bare E_2, (b) E_2-H_2O and (c) calculated spectrum of E_2-H_2O