

1D1a Laser spectroscopic study of jet-cooled non-volatile molecules combined with laser ablation

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[Introduction] Laser ablation is used to vaporize non-volatile molecules, which are decomposed by heating. In our laboratory we have been conducting supersonic jet / laser spectroscopic study for cinnamic acid derivatives. In this study, we present laser spectroscopic study of substituted cinnamic acids; sinapic acid, ferulic acid, caffeic acid, and their hydrated complexes.

[Experimental] The solid powder sample and carbon black were ground in a mortar to make fine particles. The mixed powder was attached on the surface of a graphite disk. The disk was fixed near the orifice of the pulse valve and rotated with motor. Fundamental Nd³⁺:YAG laser (1064 nm) was focused on the disk surface with a lens, and the sample on the disk surface was evaporated. At the same time of laser evaporation, Ar carrier gas was injected from the pulse valve into the vacuum, and supersonically cooled jet is obtained by the adiabatic expansion. After passing the skimmer, a molecular beam is obtained. The cooled sample in the molecular beam is irradiated by a pulsed tunable UV laser and S₁-S₀ electronic spectrum is obtained by resonant two-photon ionization (R2PI).

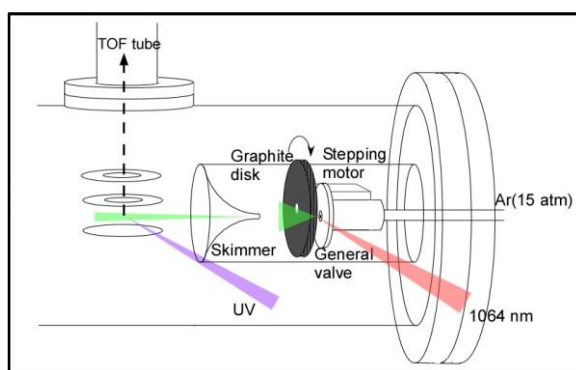


Fig.1 Experimental setup of laser ablation / supersonic beam / laser spectroscopy

[Results and discussion] Fig.2 shows the S₁-S₀ spectra of (a)caffeic acid (CA) and (b)ferulic acid (FA) in this study. A sharp spectrum was obtained in the S₁-S₀ spectrum of (b)FA. On the other hand, a very broad spectrum was obtained in the S₁-S₀ spectrum of (a)CA is very broad which is thought to be due to the very short S₁ lifetime of caffeic acid. According to the report by Domcke et al., in CA the two hydroxyl groups are hydrogen bonded and H in the acceptor O is dissociated after being excited to the S₁ state. This leads the lifetime of the S₁ state of caffeic acid very shortened.[1] In FA, dissociation of methoxy group is shorter than that of H atom of CA. We conducted a pump-probe experiment and confirmed that the S₁ lifetime of ferulic acid is very short as 15 ps. Therefore, we tried to measure sharp spectra by hydrating these acids.

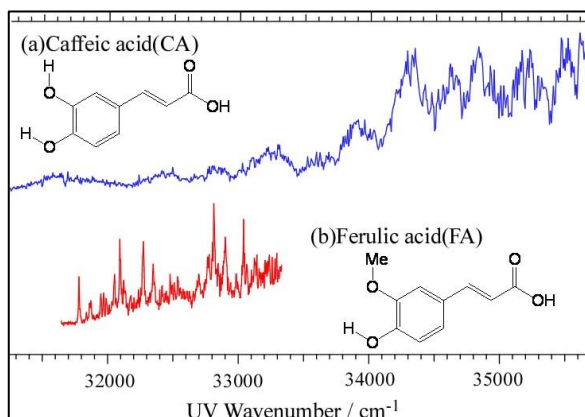


Fig.2 S₁-S₀ spectra of jet-cooled (a)caffeic acid and (b)ferulic acid

[1] N. V. Karsili, et al., J. Phys. Chem. A 2014, 118, 11999