Nonradiative Decay Route of Cinnamate Derivatives Studied by Frequency and Time Domain Laser Spectroscopy in the Gas Phase, Matrix Isolation FTIR Spectroscopy and Quantum Chemical Calculations

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The nonradiative decay route involving trans → cis photo-isomerization from the $S_1 (\pi\pi^*)$ state has been investigated for several trans-cinnamate derivatives, which are known as sunscreen reagents. We examined two types of substitution effects.

One is structural isomer such as ortho-, meta-, and para-hydroxy-methylcinnamate (o-, m-, p-HMC). The $S_1$ lifetime of p-HMC is less than 8 ps at zero-point level, and it undergoes rapid $S_1 \rightarrow {^1n\pi^*} \rightarrow T_1$ decay via multiple conical intersections. Finally, the trans → cis isomerization proceeds in the $T_1$ state. On the other hand, both o- and m-HMC show very slow decay. Their $S_1$ lifetimes are in the order of 100 ps even at the excess energy of 2000-3000 cm$^{-1}$.

The other is the effect of the complexity of ester group in para-substituted species, such as para-methoxy-methyl, -ethyl and -2ethylhexyl cinnamate (p-MMC, p-MEC, p-M2EHC). p-MMC and p-MEC show sharp $S_0 \rightarrow S_1 (\pi\pi^*)$ vibronic bands, while p-M2EHC shows only broad structureless feature even under the jet-cooled condition. In addition, we found that the $S_0 \rightarrow {^1n\pi^*}$ absorption appears at 1000 cm$^{-1}$ below the $S_0 \rightarrow S_1 (\pi\pi^*)$ transition in p-MEC and p-M2EHC, but not in p-MMC. Thus, the complexity of the ester group is very important for the appearance of the $^1n\pi^*$ state.