

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 \rightarrow 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 \rightarrow 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.