

## HYPERCONJUGATION IN THE $S_1$ STATE OF SUBSTITUTED TOLUENE PROBED BY INFRARED SPECTROSCOPY

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Internal rotation of the methyl group in substituted toluenes is one of prototypes of large amplitude motions in polyatomic molecules. The internal rotation of *o*-fluorotoluene is strongly hindered in the  $S_0$  state, but that of *m*-fluorotoluene is almost free. For the  $S_1$  state, however, the substantial changes of the internal rotation potentials have been reported; while the potential barrier in the *o*-isomer drastically decreases and the methyl group becomes almost a free rotor, the barrier in the *m*-isomer largely increases<sup>a</sup>. These surprising barrier changes have been attributed to the methyl conformation-dependent stabilization in the  $S_1$  state by the  $\pi^*$ - $\sigma^*$  hyperconjugation<sup>b</sup>. In the present study, to test this interpretation, we observed infrared spectra of *o*- and *m*-fluorotoluenes in the  $S_0$  and  $S_1$  states. Both the isomers showed decrease of the methyl CH stretch frequencies upon the electronic excitation. We concluded that this frequency decrease is the evidence of the  $\pi^*$ - $\sigma^*$  hyperconjugation.

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<sup>a</sup>K,Okuyama.;N,Mikami.;M,Ito. *J.Phys.Chem.* **1985**, 89, 5617.

<sup>b</sup>H,Nakai.;M,Kawai. *Chem.Phys.Lett* **1999**, 307, 272.