

HIGH-RESOLUTION LASER SPECTROSCOPY OF $S_1 \leftarrow S_0$ TRANSITION OF TRANS-STILBENE : NONPLANAR STRUCTURE IN THE GROUND STATE

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We have great interest in the excited-state dynamics of *trans*-stilbene such as *cis-trans* isomerization in the electronic excited state. Zewail et al. reported the results of time-resolved spectroscopy and suggested its nonplanar structure in the ground S_0 state ^a. In contrast, Pratt et al. concluded that the molecule is essentially planar both in the S_0 and S_1 states by analyzing the rotationally resolved high-resolution spectrum of the $S_1 \leftarrow S_0$ 0_0^0 band ^b. We observed the spectrum with much higher accuracy and quality, and re-determined the rotational constants by high-resolution spectrum of 0_0^0 band. Although it is impossible to accurately determine the absolute value of rotational constant A for the a -type transition, we could conclude that *trans*-stilbene is non-planar in the S_0 state. In addition to estimate the molecular structure from observed rotational constants, we developed program. By this program, we estimated that phenyl rings are rotated approximately ± 10 degrees in S_0 state. Theoretical calculation using WB97XD functional provided the phenyl rings are rotated 14 degrees in S_0 state and 2.4 degrees in S_1 state. WB97XD functional evaluate steric repulsion between H atoms of *ortho*-position in a phenyl ring and in an ethylene part by dispersion force potential semi-empirically. This result support non-planar structure revealed from the observed rotational constants.

^aJ. A. Syage, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.* **81**, 4685 (1984).

^bD. W. Pratt, W. L. Meerts et al., *J. Phys. Chem.* **94**, 6 (1990).