

HIGH-RESOLUTION LASER SPECTROSCOPY OF TRANS-STILBENE : NONPLANAR STRUCTURE IN THE GROUND STATE

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Trans-stilbene is of great interest in the excited-state dynamics 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 band ^b. We observed the spectrum with much higher accuracy and quality, and re-determined the rotational constants. Although it is impossible to accurately determine the absolute value of A for the a -type transition, we could conclude that trans-stilbene is nonplanar in the S_0 state. Theoretical calculation using WB97XD functional provided the nonplanar structure in which the phenyl rings are rotated around the C-C bond axis and take the C_2 symmetry. It suggests that steric repulsion between H atoms of *ortho*-position in a phenyl ring and in an ethylene part surpasses stabilization by π conjugation.

^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).