SINGLET-TRIPLET SPECTROSCOPY OF BUTADIENE

PAUL R. WINTER, ALLISON G. ROBINSON, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393*.

The T_1-S_0 absorption spectrum of gas phase 1,3-butadiene was recorded over the region from 20,500 to 23,000 cm^{-1} using cavity ring-down spectroscopy. The origin is located at 20,777 cm^{-1}, and several vibronic bands are observed. These bands are assigned to vibrations of a planar triplet structure based on Franck- Condon calculations. This structure has been calculated to be about 3 kcal mol^{-1} higher in energy than the twisted structure, in which one CH_2 group is oriented perpendicular to the plane of the rest of the molecule. A two-dimensional torsional calculation involving the rotation of the two terminal CH_2 groups suggests that the planar structure is located in a shallow minimum at the top of a barrier between two twisted structures.