

IDENTIFICATION OF NEW *CIS* VIBRATIONAL LEVELS IN THE S₁ STATE OF C₂H₂

J. H. BARABAN, P. B. CHANGALA, R. G. SHAVER, R. W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*; J. F. STANTON, *Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*; A. J. MERER, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*.

Although the S₁ (\tilde{A}^1A_u) state of the *trans* conformer of acetylene has been known for many years, the corresponding S₁ (\tilde{A}^1A_2) state of the *cis* conformer was only discovered recently.^a Transitions to it from the ground state are electronically forbidden, but its vibrational levels acquire intensity by tunneling through the isomerization barrier and interacting with levels of the *trans* conformer. We have recently identified two new vibrational levels (3² and 4¹6¹) of the *cis* conformer of S₁ C₂H₂, bringing the total number of levels observed to six out of an expected ten up to the energies studied in this work. The appearance of these levels in IR-UV double resonance LIF spectra will be discussed, along with their vibrational assignments. Experimentally determined vibrational parameters and *ab initio* anharmonic force fields for both the *trans* and *cis* conformers will be presented as part of the evidence supporting these assignments. These results shed new light on the vibrational level structure of both conformers in this isomerizing system.

^aA. J. Merer, A. H. Steeves, J. H. Baraban, H. A. Bechtel, and R. W. Field. *J. Chem. Phys.*, 134(24):244310, 2011.