THE PHENALENYL FREE RADICAL - A JAHN-TELLER-HERZBERG-TELLER D3H PAH

G. D. O'CONNOR, T. P. TROY, D. A. ROBERTS, N. CHALYAVI, B. FÜCKEL, M. J. CROSSLEY, K. NAUTA, T.W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*; and J. F. STANTON, *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165, United States*.

After benzene and naphthalene, the smallest polycyclic aromatic hydrocarbon bearing six-membered rings is the threefold-symmetric phenalenyl radical. Despite the fact that it is so fundamental, its electronic spectroscopy has not been rigorously scrutinized, in spite of growing interest in graphene fragments for molecular electronic applications. Here we used complementary laser spectroscopic techniques to probe the jet-cooled phenalenyl radical *in vacuo*. Its spectrum reveals the interplay between four electronic states that exhibit JahnTeller and pseudo-JahnTeller (Herzberg-Teller) vibronic coupling. The coupling mechanism has been elucidated by the application of various *ab initio* quantum-chemical techniques.