ROVIBRATIONAL LEVEL STRUCTURE OF ACETYLENE BY STIMULATED EMISSION PUMPING: CORIOLIS COUPLING BETWEEN $\nu_2 + 4\nu_4$ AND $7\nu_4$

DAVID B. MOSS, *Division of Science and Mathematics, College of General Studies, Boston University, Boston, MA 02215*; RICHARD DUAN, MATTHEW P. JACOBSON, JONATHAN P. O'BRIEN, and ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*.

Stimulated emission pumping (SEP) spectroscopy has been used to investigate the rovibrational level structure of S_0 acetylene with $0.1\,\mathrm{cm}^{-1}$ resolution at a vibrational energy of approximately $4400\,\mathrm{cm}^{-1}$. Both the e and f parity levels of the expected zero-order bright state $\nu_2 + 4\nu_4$ ($\ell = 0, 2$) are observed to be doubled by a rotationally inhomogeneous perturbation. SEP spectra obtained using S_1 intermediate levels with $K = 1$ vs. $K = 0$ reveal complementary intensity patterns, indicating that the perturbation follows a selection rule for vibrational angular momentum of $\Delta\ell$ = odd. The perturbation is assigned to a Coriolis interaction between $\nu_2 + 4\nu_4$ and the pure bending dark state $7\nu_4$. Zero-order vibrational energies and B values, as well as the Coriolis coupling coefficient, are derived from a fit of greater than 60 rovibrational levels of both parities with $J = 1$ to 13. Parameters derived from the fit are compared with predictions based on previous infrared and dispersed fluorescence studies. Axis-switching effects are also found to contribute significantly to the observed intensities.