

A HIGH RESOLUTION VIEW OF INTERSYSTEM CROSSING IN AN ISOLATED SINGLET CARBENE: STIMULATED EMISSION PUMPING SPECTROSCOPY OF CH³⁵Cl

C. MUKARAKATE, C. TAO AND S. A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233.*

Low resolution single vibronic level (SVL) emission spectra of chlorocarbene, CHCl, obtained by Chang and co-workers reveal weak transitions that have been assigned to triplet levels on the basis of high level *ab initio* calculations.^a We recently used K_a -sorted emission spectra to show that the A rotational constant of the presumed triplet origin is consistent with theoretical predictions, and observed several previously unreported triplet levels for CHCl and CDCl.^b We report in this work the first high resolution spectra of singlet-triplet transitions in CH³⁵Cl, obtained using stimulated emission pumping (SEP) spectroscopy from selected rovibrational levels in the A^1A'' state. Our spectra reveal detailed information on the rovibrational structure of the triplet state levels, and a pronounced vibrational state dependence of the spin-spin splitting, which is a sensitive probe of spin-orbit coupling with nearby singlet levels. The derived singlet-triplet gap and triplet rovibronic and spin parameters are compared with the results of recent high level *ab initio* calculations.

^aC.-S. Lin, Y.-E. Chin, and B.-C. Chang, *J. Chem. Phys.* 121, 4164 (2004).

^bC. Tao, C. Mukarakate, and S. A. Reid, *J. Chem. Phys.* 124, 224314 (2006).