A HIGH RESOLUTION VIEW OF INTERSYSTEM CROSSING IN AN ISOLATED SINGLET CARBENE: STIMULATED EMISSION PUMPING SPECTROSCOPY OF $CH^{35}Cl$

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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 $CH^{35}Cl$, 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.

[a] C.-S. Lin, Y.-E. Chin, and B.-C. Chang, J. Chem. Phys. 121, 4164 (2004).
[b] C. Tao, C. Mukarakate, and S. A. Reid, J. Chem. Phys. 124, 224314 (2006).