SINGLE VIBRONIC LEVEL EMISSION SPECTROSCOPY OF CHCl AND CDCl: VIBRATIONAL STRUCTURE OF THE X^1A' AND a^3A'' STATES

C. MUKARAKATE, C. TAO, AND S. A. REID, *Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201-1881.*

We report on single vibronic level (SVL) emission spectra from bands in the progressions 2_0^n, $2_0^n 3_0^m$, $1_0^1 2_0^n$, and $1_0^1 2_0^n 3_0^1$ in the A^1A''-X^1A' system of $CH^{35}Cl$, $CH^{37}Cl$, $CD^{35}Cl$ and $CD^{37}Cl$. As in previous studies of CHF/CDF and CHBr/CDBr, the carbenes were generated using a pulsed discharge source, and SVL emission spectra obtained using a 0.3 m spectrograph in combination with a gated, intensified CCD detector. These spectra reveal rich new detail regarding the vibrational structure of the X^1A' and a^3A'' states, and spin-orbit induced mixing between them, up to 9000 cm^{-1} above the vibrationless level of the X^1A' state. For CHCl, we observe around three times the number of X^1A' levels previously reported,[a], and a number of new a^3A'' state levels. The results of Dunham expansion fits to the vibrational term energies, and comparisons with previous experimental and recent high quality theoretical studies[b,c] will be reported. Overall, the derived vibrational parameters of the X^1A' and a^3A'' states are in excellent agreement with $ab\ initio$ predictions, including our own DFT calculations.

[a] C.-S. Lin et al., J. Chem. Phys. 121, 4164 (2004).
[b] G. Tarczay et al., Phys. Chem. Chem. Phys. 7, 2881 (2005).
[c] H.-G. Yu et al., Mol. Phys. 104, 47 (2006).