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

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We obtained single vibronic level (SVL) emission spectra following excitation of bands in the progressions 2_0^n, $2_0^n3_0^m$, $1_0^12_0^n$, and $1_0^12_0^n3_0^m$ in the A^1A''-X^1A' system of CHBr and 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 both isotopomers we observe more than twice the number of levels previously reported,[a] and the results of Dunham expansion fits to the vibrational term energies, and comparisons with previous experimental and theoretical studies, will be reported. Our results lead to several revised assignments, including the X^1A' state C-H stretching fundamental. For both isotopomers we observe almost every possible X^1A' level below 4000 cm^{-1}. Unlike CHBr, where even the lowest bending level is strongly perturbed, every level save one below 3000 cm^{-1} in CDBr is reproduced by a Dunham expansion fit to within our experimental uncertainty. However, the spin-orbit mixing is extensive above 4000 cm^{-1} in both isotopomers, and many unassigned lines remain. 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] W.-Z. Chang et al., Chem. Phys. Lett. 413, 25 (2005).