ELECTRONIC SPECTROSCOPY OF THE A\(^1\)A\(^n\)-X\(^1\)A\(^l\) SYSTEM OF CHBr AND CDBr

M. DESELNICU, C. TAO, C. MUKARAKATE AND S. A. REID, Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881.

We report a comprehensive new study of the electronic spectroscopy of the A\(^1\)A\(^n\)-X\(^1\)A\(^l\) system of CHBr and CDBr in the region 450-750 nm. For each isotopomer, more than 30 cold bands in the progressions \(2^0, 2^0\,3^0 (m=1-3), 1^24\) \& \(1^22\,3^0 (m=1-2)\) were observed, in addition to a number of hot bands. The spectra were measured under jet-cooled conditions using a pulsed discharge source, and rotationally analyzed to yield precise values for the band origins and rotational constants. The derived A\(^1\)A\(^n\) state vibrational intervals are combined in Dixon plots with the results of Sears, Muckerman, and co-workers\(^a\) to derive barriers to linearity for the \(2^0\), \(2^0\,3^1\), and \(2^0\,3^2\) progressions. The A\(^1\)A\(^n\) C-H (C-D) stretching frequency was determined for the first time, and is in excellent agreement with the predictions of \textit{ab initio} electronic structure theory.\(^b\) The observed \(\nu_3\) dependence of the CH\(^29\)Br-CH\(^81\)Br isotope splitting in the A\(^1\)A\(^n\) state is also in excellent agreement with theory.