ELECTRONIC SPECTROSCOPY OF THE A^1A''-X^1A' SYSTEM OF CHBr AND CDBr

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We report a comprehensive new study of the electronic spectroscopy of the A^1A''-X^1A' system of CHBr and CDBr in the region 450-750 nm. For each isotopomer, more than 30 cold bands in the progressions 2_0^n, $2_0^n3_0^m$ (m=1-3), $1_0^12_0^n$,and $1_0^12_0^n3_0^m$ (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^1A'' 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^n, 2^n3^1, and 2^n3^2 progressions. The A^1A'' C-H (C-D) stretching frequency was determined for the first time, and is in excellent agreement with the predictions of *ab initio* electronic structure theory.[b] The observed ν_3 dependence of the $CH^{79}Br$-$CH^{81}Br$ isotope splitting in the A^1A'' state is also in excellent agreement with theory.

[a] H.-G. Yu et al., J. Chem. Phys. 115, 5433 (2001).
[b] H.-G. Yu et al., J. Chem. Phys. 116, 1435 (2002).