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, $2_0^n 3_0^m$ (m=1-3), $1_0^1 2_0^n$,and $1_0^1 2_0^n 3_0^m$ (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, $2^n 3^1$, and $2^n 3^2$ 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).