ELECTRONIC SPECTROSCOPY, LIFETIMES, AND BARRIER TO LINEARITY IN THE $A^1B_1 - X^1A_1$ SYSTEM OF CBr_2

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Using an improved discharge recipe for the production of dibromocarbene, we report a comprehensive new study of the electronic spectroscopy of the $A^1B_1 - X^1A_1$ system of CBr_2 in the region from 525-650 nm. A total of 33 cold bands in the progressions 2_0^n (n=2-19) and $1_0^1 2_0^n$ (n=1-16) were observed. The spectra were measured under jet-cooled conditions (T_{rot} = 10 K), and rotational analysis yielded band origins and A rotational constants for all three isotopomers. The isotope shifts are in good agreement with the product rule, and, when plotted vs. bending quantum number, the measured A constants follow a linear trend except for the highest bending levels, where an abrupt increase is observed, indicating the approach to linearity. This is mirrored in the vibrational intervals, which also change abruptly in this region, and the estimated barrier height of 18 800 cm^{-1} above the vibrationless level of the X^1A_1 state is in excellent agreement with ab initio predictions of Sendt and Bacskay. [a] We also report fluorescence lifetimes as a function of vibrational level and K_a'; the lifetimes decrease rapidly with energy, but display no dependence on K_a' over the measured range. The implications of these results for understanding the excited state structure of this prototypical carbene is emphasized.

[a] K. Sendt and G. Bacskay, J. Chem. Phys. 112, 2227 (2000).