ON THE RENNER-TELLER EFFECT AND BARRIERS TO LINEARITY AND DISSOCIATION IN HCF (A^1A'')

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To further investigate the Renner-Teller effect and excited state barriers to linearity and dissociation in the simplest singlet carbene, HCF, we measured fluorescence excitation spectra and lifetimes of the pure bending transitions 2_0^n with n = 0-7 and the combination bands $1_0^1 2_0^n$ with n = 1-6 and $2_0^n 3_0^1$ with n = 0-3 in the HCF A^1A''-X^1A' system. 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 parameters are in excellent agreement with the predictions of $ab\ initio$ electronic structure theory. The approach to linearity is evidenced in a sharp increase in the A rotational constant, a minimum in the bending vibrational intervals, and a pronounced fluorescence lifetime lengthening for levels with $K_a' > 0$. A fit of the vibrational intervals for the pure bending levels yields a barrier to linearity of 6300 cm^{-1} above the vibrationless level. Our observation of the K_a' = 1 level of (1,6,0) places a lower limit on the barrier to dissociation of 8555 cm^{-1} above the vibrationless level.