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 \(2^2_0\) with \(\nu = 0-7\) and the combination bands \(1^1_2\) with \(\nu = 1-6\) and \(2^2_0\) with \(\nu = 0-3\) 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 \textit{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.