HOT BAND TRANSITIONS IN SINGLET CH_2 TO LEVELS AT THE BARRIER TO LINEARITY

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The low-lying excited singlet states of CH_2 form a Renner-Teller pair which are degenerate at linearity at an energy of 8666 cm^{-1} [a] above the minimum of the lower $\tilde{a}^1A_1$ component. While the $\tilde{b}^1B_1 \leftarrow \tilde{a}^1A_1$ electronic band system has been the subject of a large number of spectroscopic measurements, direct spectroscopic transitions to levels in the barrier energy region are weak, due to poor Franck-Condon factors, and have proved difficult to detect. In this work, we make use of hot band transitions from the first excited bending level of the lower singlet state and have characterized two, previously undetected, vibronic levels ($\tilde{b}(000)^2$, and $\tilde{a}(070)^1$) in the energy region of interest, and a third ($\tilde{a}(0,10,0)^2$) at higher energy. The measurements used a near-IR diode laser-based spectrometer to probe the singlet potential surfaces in a region not previously experimentally accessible and will help refine model calculations of the singlet methylene surfaces. In combination with previous results, a very detailed picture of the pattern of rovibronic energies resulting from the RTE can be built up. In addition, the new measurements provide more precise rotational spacings for the $\tilde{a}^1A_1(010)$ level. Observed rotational perturbations in this level will be compared to the calculated pattern of triplet state levels at the same energy in an attempt to identify specific pairs of singlet-triplet mixed states.

[a] J. -P. Gu *et al.* J. Molec. Struct. **517-518**, 247 (2000)