GAS PHASE UV EXCITATIONS OF 2-(4-)CYCLOPROPYLPYRIDINES

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The gas phase UV spectrum of 2-cyclopropylpyridine is found to include three different absorption bands: (a) an absorption tail at 320 - 290 nm, (b) a progression at 290 - 250 nm with vibrational fine structure and (c) an absorption peak at 229 nm. The long-wavelength progression is assigned to a $\Delta - \pi^*$ transition. The analysis of its fine structure shows vibration frequencies at 993 cm^{-1} and 943 cm^{-1} which are close to the ground state vibration of cyclopropane (1054 cm^{-1}). This assignment is confirmed by the photoelectron spectrum of the same molecule, which shows that both Walsh molecular orbitals (MOs) are energetically the highest with energies of 8.8 and 9.4 eV respectively, and by a second order perturbation treatment of the interaction of cyclopropane and pyridine MOs. The nature of the other two bands, $n-\pi^*$ and $\pi - \pi^*$, is determined by considering their behaviour in measurements with solvents of different polarities and pH values.

Similar analysis of the gas phase UV spectrum of 4-cyclopropylpyridine yields three different bands which may be assigned in the same manner as $n-\pi^*$ (320-280 nm), $\Delta - \pi^*$ (260 nm) and $\pi - \pi^*$ (226 nm). However, no distinct fine structure for the $\Delta - \pi^*$ band can be detected. The $n-\pi^*$ and $\pi - \pi^*$ nature of the other two bands is assigned considering their behaviour in different solutions and pH values too.