A NEW INTERPRETATION OF THE ELECTRONIC SPECTRUM OF ETHYLENE IN THE 6-8 eV REGION

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The traditional assignment of the electronic spectrum of ethylene in terms of a π-π* N-V excitation and an overlapping π-3s Rydberg excitation is shown to be inconsistent with the oscillator strengths calculated and observed for these transitions. A spectral intensity calculation based on intersecting N-V (B_{1u}) and π-$3p_y$ (B_{1g}) surfaces, as proposed by Petrongolo et al. [J. Chem. Phys. 76, 3655 (1972)], is shown to result in a vibronic spectrum in reasonable agreement with experiment. This revised assignment provides much better overall agreement between theory and experiment than the traditional assignment for which, it is argued, there is no convincing evidence. Recent calculations of the absorption spectrum expected on the basis of ab initio treatments that include both torsion and stretch will be presented. Experimental methods for the location of the π-3s (allowed) transition will be discussed.
Reference: Jae-seok Ryu and Bruce S. Huson, Chem. Phys. Lett. 245, 448-454 (1995).