

PROGRESS INVESTIGATING A MYSTERY CONCERNING THE $\pi-\pi^*$ ELECTRONIC TRANSITION IN ETHYLENE AND OTHER DOUBLE BONDED MOLECULES

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If the electronic structure of a molecule is completely known, then the chemistry [all interactions, properties, and reactions] is determined. It is of particular importance to understand the electronic structure of the simplest olefin, ethylene [$\text{H}_2\text{C}=\text{CH}_2$]. Ethylene is not only important in its own right but serves as the basis for understanding the carbon-carbon double bond chromophore, which is ubiquitous in chemistry and biochemistry. For ethylene, it has always been believed and even taught in undergraduate courses that the $\pi-\pi^*$ (${}^1\text{A}_g \Rightarrow {}^1\text{B}_{1u}$) electronic transition is the lowest energy electronic transition. Unfortunately there have always been problems associated with this interpretation. [See references in reference 1.] This mystery has been the impetus for these investigations.

Magnetic circular dichroism [MCD] measurements give unique information about the electronic structure of a molecule. Professor Snyder et al. developed an instrument capable of vacuum ultraviolet [VUV] absorption and MCD measurements using synchrotron radiation at the Synchrotron Radiation Center. VUV MCD and absorption measurements on ethylene and methylethylene have shown that the lowest energy transition is not $\pi-\pi^*$, but the $\pi-3s$ (Rydberg) (${}^1\text{A}_g \Rightarrow {}^1\text{B}_{3u}$) transition.¹ Another surprise was the near degeneracy of the $\pi-3p$ transition(s) [$\pi \Rightarrow 3p_\sigma$ (${}^1\text{A}_{1g} \Rightarrow {}^1\text{B}_{2g}$) and/or the $\pi \Rightarrow 3p_y$ (${}^1\text{A}_{1g} \Rightarrow {}^1\text{B}_{1g}$)] with the $\pi-\pi^*$ transition.

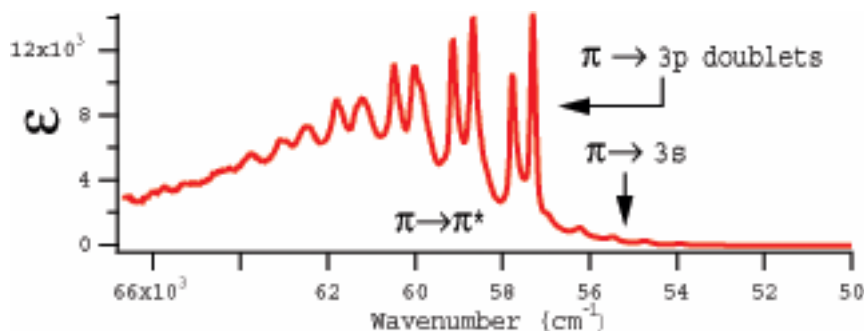


Figure 1: VUV Absorption Spectrum Showing the New Assignments for Ethylene.

To further understand and investigate the electronic structure of ethylene and other olefins, experimental measurements have been carried out on 1,1-dimethylethylene. Preliminary results will be presented.

The experimental results on these fundamental molecules are absolutely vital for determining which quantum mechanical assumptions give the correct results as well as understanding the many properties and interactions of the double bonded chromophore.

Reference: 1. P.A. Snyder, S. Atanasova, R.W.C. Hansen, *J. Physical Chemistry A* **2004**, 108, 4194.

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