

## Effects of Wave Function Modifications on Calculated HC and CC Stretching Frequencies in $\text{H}_2\text{C}=\text{CHX}$ and $\text{HC}\equiv\text{CHX}$ Molecules

Mozart N. Ramos<sup>1</sup>, Kelson C. Lopes<sup>2</sup>, Victor H. Rusu<sup>1</sup>, Regiane C.M.U. Araújo<sup>2</sup>

<sup>1</sup>*Departamento de Química Fundamental, Universidade Federal de Pernambuco (UFPE), 50739-901, Recife (PE), Brasil,*

<sup>2</sup>*Departamento de Química, Universidade Federal da Paraíba (UFPB), 58036-300, João Pessoa (PB), Brasil*

Two-level factorial designs (FD) have been used to determine the effects of wave function modifications on calculated CH and CC harmonic stretching frequencies of the  $\text{H}_2\text{C}=\text{CHX}$  and  $\text{HC}\equiv\text{CHX}$  molecules with X= H,  $\text{CH}_3$ , F, Cl and CN. These modifications were treated at two levels, which consists in: (I) using either a double- or a triple-zeta valence basis set; (II) including or not diffuse functions in basis set, (III) including or not polarization functions in basis set, and (IV) performing a calculation with or without electron correlation beyond the Hartree-Fock level, i.e., MP2 or B3LYP. Our results have shown that valence (VAL), diffuse (DIF), polarization (POL) and electron correlation (CORR) principal effects as well as some second-order interaction effects are significant to build factorial models for these vibrational modes. When valence and diffuse functions are introduced in the basis set, the calculated HC and CC stretching frequencies are decreased in both the  $\text{HC}\equiv\text{CHX}$  and  $\text{H}_2\text{C}=\text{CHX}$  molecules. For instance, when diffuse functions are used in the basis set, the reductions in  $\nu_{\text{HC}}$  and  $\nu_{\text{CC}}$  are  $-9.0\text{ cm}^{-1}$  and  $-13.2\text{ cm}^{-1}$  in  $\text{HC}\equiv\text{CHX}$ , whereas their corresponding values in  $\text{H}_2\text{C}=\text{CHX}$  are  $-4.1\text{ cm}^{-1}$  and  $-13.8\text{ cm}^{-1}$ , respectively. However, these reductions are much more accentuated when the electron correlation effect is introduced in the Hartree-Fock wave functions. As expected, by far the correlation principal effect is the most important on the frequency values. This effect provokes a decrease of  $-281.4\text{ cm}^{-1}$  and  $-153.5\text{ cm}^{-1}$  in the  $\text{C}\equiv\text{C}$  and  $\text{C}=\text{C}$  vibrational frequencies, respectively, using the MP2 calculations, whereas this decrease for the H-C oscillator is  $-156.1\text{ cm}^{-1}$  and  $-116.1\text{ cm}^{-1}$  in  $\text{HC}\equiv\text{CHX}$  and  $\text{H}_2\text{C}=\text{CHX}$  respectively. This same effect produces an important POL-CORR interaction effect on HC and CC stretching frequencies, increasing their values by  $+45.3\text{ cm}^{-1}$  and  $+18.4\text{ cm}^{-1}$  in  $\text{HC}\equiv\text{CHX}$ , respectively, whereas their corresponding values in  $\text{H}_2\text{C}=\text{CHX}$  are  $+43.9\text{ cm}^{-1}$  and  $+11.0\text{ cm}^{-1}$ , respectively. Finally, algebraic models were then established to explain how calculated HC and CC stretching frequencies in  $\text{HC}\equiv\text{CHX}$  and  $\text{H}_2\text{C}=\text{CHX}$  depend on the characteristics of the molecular orbital wave functions.