Theoretical study of the photoelectron spectra of 2-butynoyl fluoride and 2-butynal

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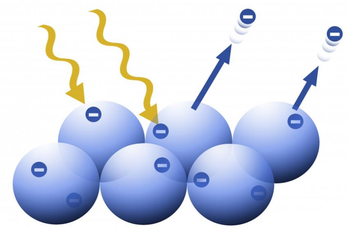
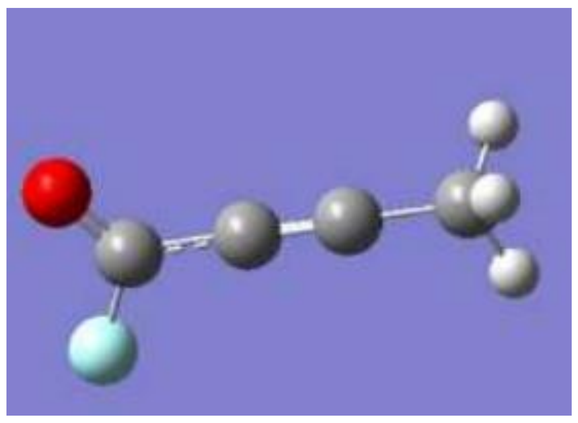


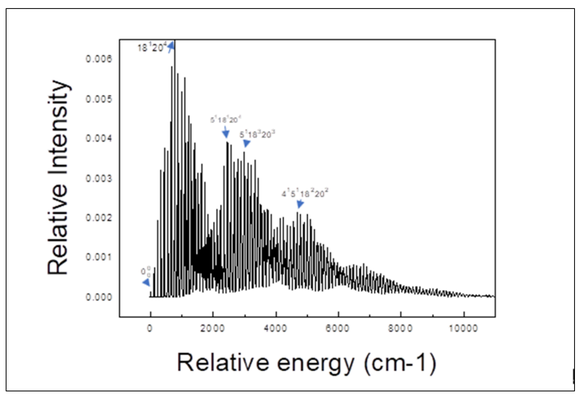
Abstract

The equilibrium structures and vibrational frequencies of 2-butynoyl fluoride (**1**) and 2-butynal (**2**) and their cations were computed with the B3LYP, PBE0, ωB97XD, and APFD approaches in conjunction with the aug-cc-pVTZ basis set. A hybrid model of harmonic and anharmonic oscillators developed by our group was used to calculated the Franck–Condon factors,[1] from which the photoelectron spectra of these two molecules were simulated. The vibrational structure in the photoelectron spectrum of **1** is complex involving a large number of vibrational excitations. In contrast, fewer excitations of **2** are predicted, in which the primary transitions correspond to the origin band and the ν_6, ν_{11} and ν_{15} transitions. The predicted photoelectron spectra of **1** and **2** are in harmony with the experimental spectra reported in the literature.[2]

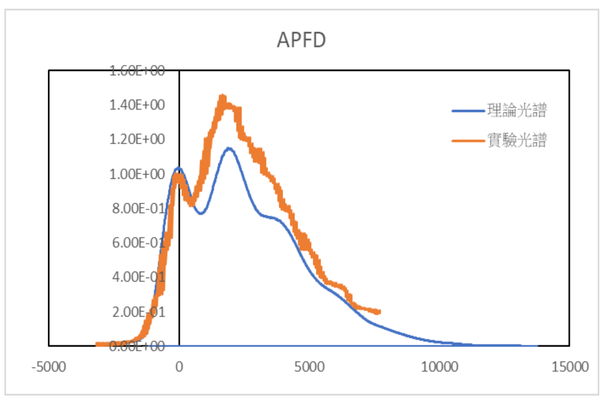
Results and Discussion

The research of 2-butynoyl fluoride

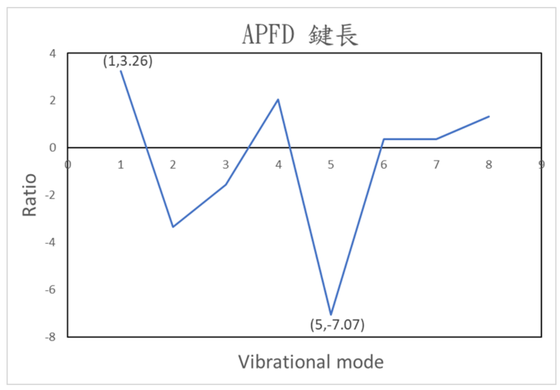




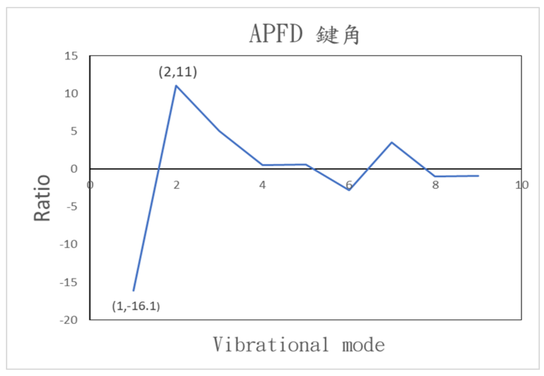
Theoretical spectrum (APFD)



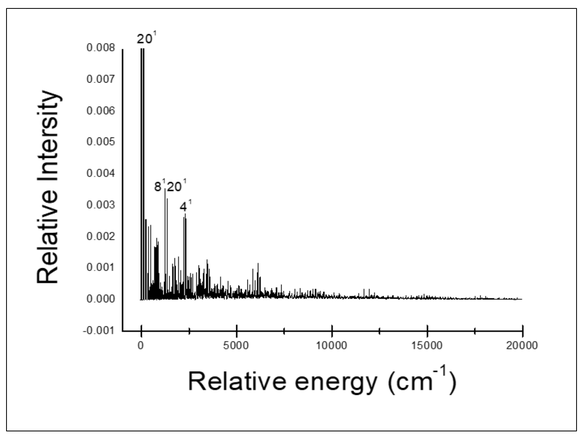
Theoretical vs. experimental spectra[2]



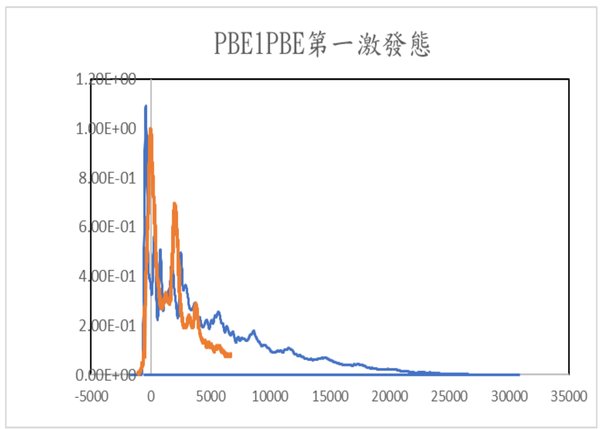
Change of bond lengths upon ionization



Change of bond angles upon ionization

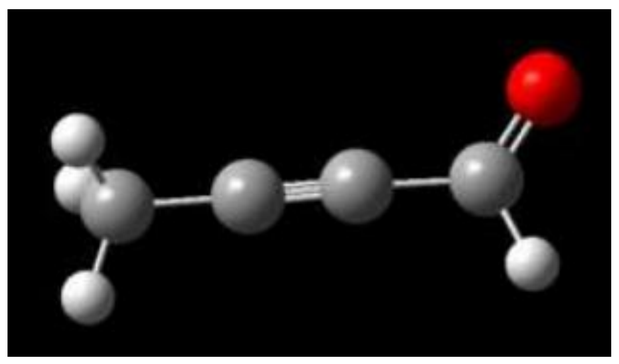


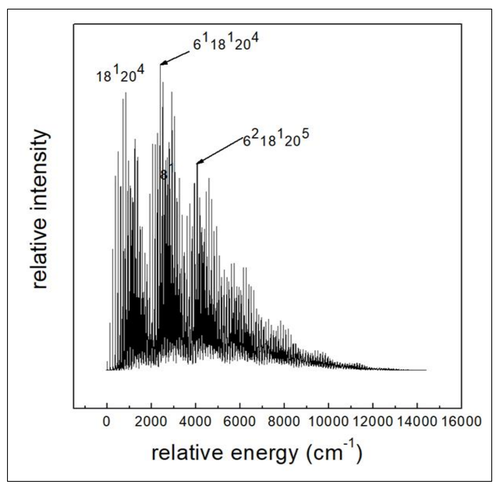
Theoretical photoelectron spectrum of the first excited state (PBE0)



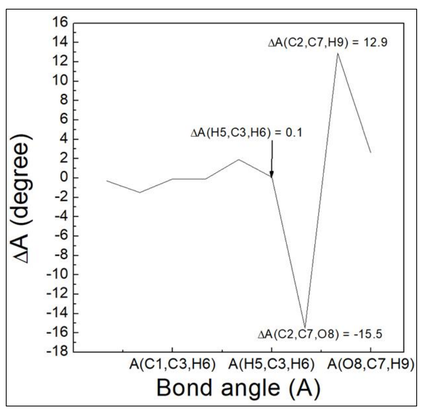
Theoretical vs. experimental spectra[2] of the first excited state

The research of 2-Butynal

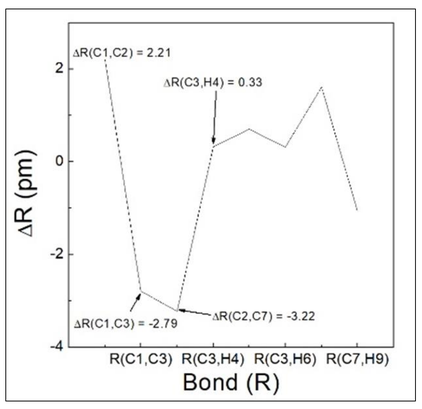




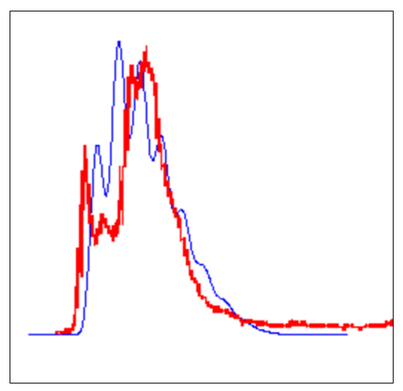
Theoretical spectrum (B3LYP)



Change of bond angles upon ionization



Change of bond lengths upon ionization



Theoretical vs. experimental spectra[2]

References

1. Chang, J.-L.; Chen, H.-Y.; Huang, Y.-J., Reassignment of the Photoelectron Spectrum of Methylketene Using a Hybrid Model of Harmonic and Anharmonic Oscillators to Compute Franck–Condon Factors. *ACS Omega*, **2023**, *8*, 40685-40694.
2. Klapstein, D.; O'Brien, R. T., The He(I) photoelectron spectra of 2-butynal and related oxyalkynes. *Canadian Journal of Chemistry*, **1988**, *66*, 143-148.