OBSERVATION AND *AB INITIO* CALCULATION OF THE TWO-PHOTON VIBRONIC SPECTROSCOPY OF JET-COOLED ALLENE AND PROPYNE

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The two-photon allowed vibronic spectra of jet-cooled allene (H_2CCCH_2) and propyne (H_3CCCH) at 7.5-9 eV have been observed by $2+1$ REMPI spectroscopy. Excited electronic states of 2^1A_1 (π-3p/π-π^*), 2^1A_2 (π-3p), 2^1B_1 (π-3p) and 3^1A_1 (π-3d/π-π^*) in allene and $^1A_2$ (π-π^*) in propyne are responsible for the observed spectra according to recent *ab initio* calculations. Geometries of the singlet excited electronic states of allene and propyne have been optimized at the CASSCF level of theory with the 6-311(2+)G** basis set. Vertical and adiabatic excitation energies, calculated by the MRCI and EOM-CCSD methods are compared with experiment. Vibrational frequencies and normal coordinates for the ground and excited states are used for the calculations of vibrational overlap integrals and Franck-Condon factors, taking into account distortion, displacement and normal mode mixing (Duschinsky matrix), as we demonstrated previously in the ethylene case.[a,b] Major features of the observed vibronic spectra of allene and propyne will be interpreted on the basis of computed Franck-Condon factors. REMPI spectra to cover the energy range of 6 eV to ionization potential are undertaken.

[a] A. M. Mebel, Y.-T. Chen and S. H. Lin, Chem. Phys. Lett., **258**, 53 (1996).
[b] A. M. Mebel, Y.-T. Chen and S. H. Lin, J. Chem. Phys., **105**, 9007 (1996).