HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPIC STUDY OF CYCLOPROPENE (c-C_3H_4)

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The spectroscopic information available on the cyclopropene radical cation is limited to that contained in low-resolution He I photoelectron spectra [a,b]. To better characterize the structure of this cation, we have recently measured high-resolution PFI-ZEKE photoelectron spectra of c-C_3H_4 and several of its deuterated isotopomers in the vicinity of the adiabatic ionization threshold. Our new data include fully rotationally resolved spectra of the origin band of the $\widetilde{X}^+ \leftarrow \widetilde{X}$ transition of c-C_3H_4 and spectra of the low-vibrational levels of c-C_3H_4 and the deuterated isotopomers recorded at lower resolution. Because our efforts at synthesizing the partially deuterated isotopomers always resulted in mixtures of several isotopomers, differing in their number of D atoms and in the location of these atoms, the analysis of the isotopic shifts turned out to be challenging. Combining the information contained in the rotational structure of the origin band of c-C_3H_4 with the ionization energies of the isotopomers measured by photoionization mass spectrometry and the vibrational structure observed in the PFI-ZEKE spectra of the mixtures of deuterated isotopomers, we were able to draw conclusions on the structure of the cyclopropene radical cation based solely on experimental data. The adiabatic ionization energy of c-C_3H_4 was determined to be $77931.8(5)\,\mathrm{cm}^{-1}$.

[a] M. B. ROBIN, C. R. BRUNDLE, N. A. KUEBLER, G. B. ELLISON AND K. B. WIBERG, *J. Chem. Phys.* **57**, 1758 (1972).
[b] P. BISCHOF AND E. HEILBRONNER, *Helv. Chim. Acta* **53**, 1677 (1970).