STRUCTURE AND DYNAMICS OF THE CYCLOPROPENE RADICAL CATION STUDIED BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY

KONSTANTINA VASILATOU, JULIE M. MICHAUD, DENITSA BAYKUSHEVA, GUIDO GRASSI and FREDERIC MERKT, *Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093 Zürich, Switzerland*.

High-resolution photoelectron spectra of cyclopropene (c-C_3H_4) and several of its deuterated isotopomers have been recorded. From the analysis of the almost fully resolved rotational structure of the origin of the $\widetilde{\mathrm{X}}^{+\,2}\mathrm{B}_2 \leftarrow \widetilde{\mathrm{X}}\,^1\mathrm{A}_1$ ionizing transition of c-C_3H_4, c-C_3H_3D, c-$C_3H_2D_2$, c-C_3HD_3 and c-C_3D_4 and the observation of several low-lying vibrational levels of the corresponding cations, we conclude that the cyclopropene cation has an equilibrium structure deviating from $C_{2\mathrm{v}}$ symmetry. We believe that the cation is subject to a large-amplitude tunnelling motion along a mode of a_2 symmetry involving a twist of the CH_2 group and an asymmetric out-of-plane bending of the CH units. The reasons for this belief and also currently unresolved aspects of our analysis will be discussed.