HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPIC STUDY OF THE FIRST TORSIONAL LEVELS OF THE ALLENE CATION

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The pulsed-field-ionisation zero-kinetic-energy photoelectron spectrum of allene has been recorded in the region near the origin of the $\widetilde{X} \rightarrow \widetilde{X}^+$ transition with a resolution of better than 0.2 cm^{-1}. The spectrum reveals a dominant vibrational progression in the torsional mode ν_4 and several weaker vibrational bands. The rotational structure of these bands is almost fully resolved.
In the origin band and the first excited torsional band line positions as well as line intensities was analyzed in order to determine structural parameters of the $C_3H_4^+$ ion and to understand the photoionization dynamics of allene. The rovibronic intensity distribution suggests a distortion from the D_{2d} structure in the cation with negligible tunneling for the lowest two torsional bands (v_4=0 and 1). The spectral intensities could be quantitatively reproduced using the recent model of Willitsch et al. [1] on the assumption that the electron is ionized out of a molecular orbital that can be represented by a linear combination of p_π and d_π components in a single centre expansion, whereby π refers to the projection of the orbital angular momentum onto the main axis.
Higher vibrationally excited bands were also recorded, revealing a more complex rotational structure indicative of a rovibrational interaction in this region.