NEGATIVE ION PHOTOELECTRON SPECTRA OF DIHALOCARBENES AND DIHALOMETHYL RADICALS

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Dihalocarbenes of the form CX_2 (X = F, Cl, Br, I) are important intermediates in organic reactions, due to the unique chemical properties of their low-lying neutral singlet $^1A_1$ and triplet $^3B_1$ states that affect their reactivities. Disagreement between experimental and theoretical results for the singlet-triplet splittings in CCl_2^-, CBr_2^-, and CI_2^- prompted a careful reinvestigation of the photoelectron spectra of these compounds, revealing contamination from HCX_2^- species. Contributions from contaminants previously obscuring the dihalocarbene $^3B_1$ triplet spectra have been minimized, and photoelectron spectra of isolated HCX_2^- compounds were collected to further elucidate the dihalocarbene experimental data. The new CCl_2^- 351 nm photoelectron spectra exhibit vibrationally resolved transitions to singlet and triplet electronic states; careful analysis drastically alters the previous identification of the triplet state origin, resulting in substantially improved agreement with high level calculations.

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