

## NEGATIVE ION PHOTOELECTRON SPECTRA OF DIHALOCARBENES AND DIHALOMETHYL RADICALS

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Dihalocarbenes of the form CX<sub>2</sub> (X = F, Cl, Br, I) are important intermediates in organic reactions, due to the unique chemical properties of their low-lying neutral singlet <sup>1</sup>A<sub>1</sub> and triplet <sup>3</sup>B<sub>1</sub> states that affect their reactivities. Disagreement between experimental and theoretical results for the singlet-triplet splittings in CCl<sub>2</sub><sup>-</sup>, CBr<sub>2</sub><sup>-</sup>, and Cl<sub>2</sub><sup>-</sup> prompted a careful reinvestigation of the photoelectron spectra of these compounds, revealing contamination from HCX<sub>2</sub><sup>-</sup> species. Contributions from contaminants previously obscuring the dihalocarbene <sup>3</sup>B<sub>1</sub> triplet spectra have been minimized, and photoelectron spectra of isolated HCX<sub>2</sub><sup>-</sup> compounds were collected to further elucidate the dihalocarbene experimental data. The new CCl<sub>2</sub><sup>-</sup> 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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