FINDING THE ELUSIVE IODOCARBENE: FLUORESCENCE EXCITATION AND SINGLE VIBRONIC LEVEL EMISSION SPECTROSCOPY OF CHI

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Among the triatomic halocarbenes, only the iodocarbenes remain to be characterized. The search for these elusive species is motivated by a controversy regarding the multiplicity of the ground state. Photoelectron spectra of Lineberger and co-workers [a] suggest a triplet ground state for CHI, at variance with recent *ab initio* studies, which suggest a singlet ground state with a singlet-triplet gap of around 4 kcal mol^{-1}. In this work, we have succeeded in finding the spectra of CHI and its deuterated isotopomer using pulsed discharge jet spectroscopy. Rotationally resolved fluorescence excitation spectra are consistent with a singlet-singlet transition, and the derived rotational constants are in good agreement with theoretical predictions. Single vibronic level emission spectra confirm a singlet multiplicity for the ground state, and reveal extensive mixing of the singlet and triplet levels at higher energy. We are able to set a lower limit on the singlet-triplet gap of 4.1 kcal mol^{-1}, in excellent agreement with theory. Extrapolation of the observed bending levels for CHI and CDI to a common origin suggests that the origin of the A^1A'' state lies near 10 500 cm^{-1}, and we will report on high resolution measurements near the electronic origin made at Brookhaven National Laboratory.

[a] M. K. Gilles, K. M. Ervin, J. Ho, and W. C. Lineberger, J. Phys. Chem. 96, 1130 (1992).