STILL SEARCHING FOR THE LOW-LYING TRIPLET STATE OF CCl_2

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At the last Symposium some of the authors have presented the laser induced dispersed fluorescence (DF) spectrum of CCl_2.[a] The analysis of this spectrum yielded well-defined values for the harmonic and anharmonic constants for the symmetric ground state vibrations of the singlet electronic ground state. Irregular line positions at around 14.5 kcal mol^{-1} was interpreted as a perturbation possibly due to the low-lying triplet state. This value was much closer to the latest theoretical predictions than the one deduced from the photodetachment spectra,[b] and hence it supported the alternative interpretations[c] of the photodetachment data. However, due to the complexity of DF spectra in the higher energy regions it was not possible to give a definitive value for singlet-triplet gap. Furthermore, the 14.5 kcal mol^{-1} still shows only moderate agreement with the best theoretical predictions (19.5$\pm$2 kcal mol^{-1}[d] and 20$\pm$1 kcal mol^{-1}[e]).
One of the purposes of this work was to refine the theoretical value and get the best possible predictions for the singlet-triplet energy separation. To achieve this goal state-of-the-art theoretical techniques have been employed, including Focal Point Analysis, which involves the determination of small and auxiliary corrections, like relativistic, quantum electrodynamics and Diagonal Born-Oppenheimer corrections. To help the assignments of the experimental spectra accurate potential energy surfaces have been calculated for both the singlet and the triplet states. Using these surfaces vibrational energy levels were calculated variationally and were compared to the observed values.

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