

AB INITIO STUDY OF THE TRICHLORINE RADICAL, Cl₃

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We report a rigorous *ab initio* study of the ground and low-lying excited-state potential energy surfaces (PES) of the Cl₃ radical at CASSCF, CASPT2, and internally contracted (IC) MRSDCI levels of theory with the Dunning's *avdz* and *avtz* basis sets. (There is a previous study ^a which examined only restricted areas of the PES.) The ground state PES has two true minima, both of which are van der Waals complexes between Cl and Cl₂. The linear asymmetric minimum is of ²Π symmetry, and the bent asymmetric minimum is ²A'. At the ICMRSDCI/*avdz* level of theory with counterpoise correction for energy, the Jacobi coordinates for the linear minimum are: **r**=3.90 au, **R**=8.47 au, **D_e**(Cl₂(X)-Cl)= 250 cm⁻¹, and those of the bent minimum are: **r**=3.90 au, **R**=6.85 au, **γ**=66.47°, **D_e**(Cl₂(X)-Cl)=230 cm⁻¹. Addition of spin-orbit interaction as a perturbation predicts that the global minimum is linear ²Π_{3/2} stabilized by 280 cm⁻¹ whereas bent ²E_{1/2} is stabilized by only 136 cm⁻¹.

Excited valence states exhibit only one strongly bound minimum: ²Π_g with the bond length of 4.67 au at the ICMRSDCI/*avdz* level of theory. This state is located 1.1 eV above the van der Waals minima and exhibits a strong (1 au) dipole transition moment to the below-lying ²Π_u state. It is bound by approximately 5,000 cm⁻¹ with respect to Cl₂(³Π_u)-Cl asymptote. This minimum is due to the avoided crossing between two valence bond structures: Cl-Cl Cl and Cl Cl-Cl.

Attempts are made in connection to previous experimental and *ab initio* studies to explain the on-going hypothesis of a long-lived ground state intermediate formed by the reaction: Cl₂ + Cl ⇌ Cl₃. According to our ground state calculations this postulate is strongly undermined. In addition, we attempt to explain a 470 nm long-lived laser-induced fluorescence observed after isolating Cl and Cl₂ in Ar matrix. Our calculations do not show any evidence that the trichlorine radical is responsible for this fluorescence. However, the possibilities of Cl₃ playing some role in this process are examined.

^aA. B. Sannigrahi and Sigrid D. Peyerimhoff, *Int. J. Quantum Chem.* **30**, 413-420 (1986).