We report a rigorous ab initio study of the ground and low-lying excited-state potential energy surfaces (PES) of the Cl$_3$ 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 Cl$_2$. The linear asymmetric minimum is of $^2\Pi$ symmetry, and the bent asymmetric minimum is $^2\Sigma^+$. At the IC MRSDCI/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, $D(\text{Cl} \cdot \text{Cl})=250$ cm$^{-1}$, and those of the bent minimum are: $r=3.90$ au, $R=6.85$ au, $\gamma=66.47^\circ$, $D(\text{Cl} \cdot \text{Cl})=230$ cm$^{-1}$. Addition of spin-orbit interaction as a perturbation predicts that the global minimum is linear $^2\Pi_{3/2}$ 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: $^3\Pi_g$ with the bond length of 4.67 au at the IC MRSDCI/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 $^3\Pi_u$ state. It is bound by approximately 5,000 cm$^{-1}$ with respect to Cl$_2$($^3\Pi_u$)-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 ongoing hypothesis of a long-lived ground state intermediate formed by the reaction: Cl$_2$ + Cl $\Leftrightarrow$ Cl$_3$. 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 Cl$_2$ in Ar matrix. Our calculations do not show any evidence that the trichlorine radical is responsible for this fluorescence. However, the possibilities of Cl$_3$ playing some role in this process are examined.

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