AB INITIO STUDY OF THE TRICHLORINE RADICAL, Cl_3

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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 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 $^2A'$. 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, $\mathbf{D}_e$(Cl_2(X)-Cl)= 250 cm^{-1}, and those of the bent minimum are: **r**=3.90 au, **R**=6.85 au, γ=66.47^o, $\mathbf{D}_e$(Cl_2(X)-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: $^2\Pi_g$ 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 $^2\Pi_u$ state. It is bound by approximately 5,000 $\mathrm{cm}^{-1}$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 on-going 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.

[a] A. B. Sannigrahi and Sigrid D. Peyerimhoff, Int. J. Quantum Chem. **30**, 413-420 (1986).