Binding of oxygen with titanium dioxide on singlet potential energy surface: An *ab initio* investigation

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Titanium dioxide (TiO_2) based materials are most widely used catalysts in the fields of photocatalytic water splitting and hydrogen production, photoelectrochemistry, dye sensitization and solar energy conversion, and photochemical air and water treatments. Oxidative processes on the surface of photocatalyst proceed with participation of oxygen. It is known that singlet oxygen is generated when TiO_2 is UV-irradiated in the presence of oxygen [1]. In the presented work *ab initio* calculations within MP2/6-311+G(2d,2p) approach have been carried out to investigate interaction of titanium dioxide TiO_2 with oxygen O_2 in excited singlet states. On a singlet potential energy surface (PES) barrierless formation of the earlier unknown stable compound of titanium peroxide TiO_4 is revealed. Its structure is shown in Figure 1. This peroxide is found to be lower in energy than the ground state of two individual molecules TiO_2+$^3O_2$ by 34.6 kcal/mole. On a triplet potential energy surface weakly bound van der Waals (vdW) complex is located. The conical intersection shown in Figure 1 was found which connects this triplet vdW complex with singlet state of peroxide TiO_4.

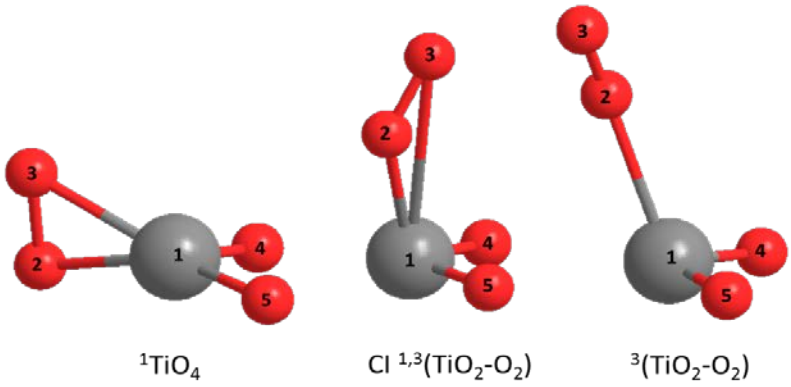

Figure 1. Structure of the ground (triplet) van der Waals complex $^3(TiO_2\text{-}O_2)$ and ground (singlet) state of titanium peroxide $^1TiO_4$ as well as conical intersection of triplet and singlet states of TiO_2-O_2 system CI $^{1,3}(TiO_2\text{-}O_2)$. In the initial pair TiO_2-O_2 oxygen atoms 4,5 belong to TiO_2 and atoms 2,3 belong to O_2.

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References:

[1] Y. Nosaka, T. Daimon, A.Y. Nosaka, Y. Murakami, *Phys. Chem. Chem. Phys*. **2004**, 6, 2917.