A QUANTUM CHEMICAL STUDY OF PHOTOCHEMICAL PROCESSES IN THE REACTION \( \text{Se} + \text{O}_2 \rightarrow \text{SeO}_2 \) WITH ALLOWANCE FOR THE SPIN ORBIT INTERACTION

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DFT, SA-MCSCF, and MRMP/MCQDPT2 methods in the 6-311++G(2d) basis set are employed to consider the features of the formation reaction of key intermediates (SeOO, Se(O₂)) and photochemical dissociation of selenium dioxide with the formation of singlet oxygen. The cross-sections of potential energy surfaces of SeO₂, Se(O₂), and SeOO are constructed and the terms of their ground and excited states are analyzed at the SeOO dissociation limit with regard to spin-orbital interaction. Possible formation channels of \( ^1\text{O}_2 \left( ^1\Delta_g, \, ^1\Sigma_g^+ \right) \) reactive oxygen species during the decay of the excited states of selenium oxocomplexes are revealed. The effect of the spin-orbit interaction on the character of electronic spectrum transitions and zero field splitting in oxygen is estimated.

Keywords: potential energy surface cross-section, excited selenium oxocomplexes, singlet oxygen, spin-orbit interaction, zero field splitting parameters.

INTRODUCTION

Selenium is a toxic substance. Its excess may result in loss of hair and nails, nervous system disorders, and other diseases [1-3]. However, selenium is vital for the normal functioning of the organism. For example, selenium deficit causes muscle disorders (Keshan disease) [4]. Drugs with low-doses of selenium can decrease or neutralize the poisonous effect on a human organism of metals such as cadmium, copper, and mercury [5] and also be a preventive measure against some cancer types.

Selenium dioxide \( \text{SeO}_2 \) and metastable excited \( \text{Se}–\text{O}_2 \) intermediates [6, 7] as well as superoxo- and peroxocomplexes of transition metals [8, 9] have excessive energy and enhanced reactivity. It is unknown whether the decay of these systems can be accompanied by the formation of reactive oxygen species (ROS) or not, e.g. singlet \( ^1\text{O}_2 \left( ^1\Delta_g, \, ^1\Sigma_g^+ \right) \) that can act both negatively on healthy cells and positively by killing carcinomas.

The properties of \( \text{SeO}_2 \) selenium dioxide in the gas phase and inert matrices were studied experimentally in [10-19]. The studies on the geometric structures of selenium oxygen clusters are presented in [20-27]. Along with \( \text{SeO}_2 \) selenium dioxide, an intermediate in the form of SeOO superoxocomplex of \( \text{C}_5 \) symmetry were found experimentally [17].

Using DFT and \textit{ab initio} methods, Grein [18] theoretically calculated the geometric structure, vertical and adiabatic excitation energies, and fundamental vibrational frequencies for 20 excited states of \( \text{SeO}_2 \) dioxide and ground states of
superoxo- (SeOO, \(C_1\)) and peroxocomplexes (Se(O\(_2\)), \(C_2\)). The geometric structure, thermochemistry, and electron affinity in Se\(_n\) clusters \((n = 1-5)\) and their anions were studied theoretically in 2008 [19].

Data on the cross-section curves of the potential energy surface (PES) of the reaction Se + O\(_2\) are absent in the literature. The terms of the ground and excited states of SeOO superoxide and Se(O\(_2\)) peroxide were not analyzed. The stability of SeOO and Se(O\(_2\)) and the activation barriers in SeOO ↔ Se(O\(_2\)) ↔ SeO\(_2\) transitions have not previously been estimated. The dissociation limits of the intermediates and intersections of PES terms are also unknown. There are no data on the ROS formation during photoactivation of SeO\(_2\) dioxide molecules or deactivation of excited SeOO and Se(O\(_2\)) oxocomplexes.

Moreover, the spin-orbit interaction (SOI) makes it possible to reveal the PES features in the formation or dissociation of intermediates. The construction of terms with a particular quantum number of the total mechanical momentum \(J_z\) and \(m\), projections on the dissociation limit in the pre-reaction zone of the collision complex (before the activation barrier of the reaction Se + O\(_2\) → Se(O\(_2\)), SeOO) provides the opportunity of a detailed analysis from which triplet sublevels of intermolecular SeOO interaction fragments and Se(O\(_2\)) intermediates form in the ground and excited states. The obtained knowledge will help predict and control the yield of desired products in the selective population of triplet sublevels of the fragments.

The purpose of the work was to clarify the features of the photochemical formation reaction of the key intermediates (SeOO and Se(O\(_2\))) and dissociation of selenium dioxide with the formation of singlet oxygen, the terms of their ground and excited states, the SOI effect on the character of electronic spectrum transitions and zero field splitting (ZFS) in oxygen.

Therefore, we had to construct PES cross-sections of electronic terms, to estimate the dissociation energy of Se–O and O–O bonds in the first excited states of SeO\(_2\) dioxide and also in the ground and first excited states of Se(O\(_2\)) peroxide and SeOO superoxide, and to calculate the activation barriers of the forward and back reactions in SeOO superoxide ↔ Se(O\(_2\)) peroxide and SeO\(_2\) dioxide ↔ Se(O\(_2\)) peroxide transitions. It was especially important to analyze the region of dissociation limits using the constructed PES curves, i.e. to answer the question: from which excited states of the selenium atom and molecular oxygen one or another metastable complex may form and to what fragments the superoxocomplex can dissociate (adiabatically, non-adiabatically) with and without allowance for SOI. The knowledge of the relative arrangement of electronic terms and their intersections helps us to predict the ROS formation in dissociation of the excited states of dioxide, peroxide, and superoxide.

**CALCULATION METHODS**

A theoretical description of the ground and excited states of metastable Se–O\(_2\) intermediates is very difficult. Quite recently, in 2008-2009, high-precision calculations of the geometric and spectral characteristics of the ground and first excited states of OSeO selenium dioxide were performed by DFT/B3PW91/6-311+G(3\(d\)\(f\)), CCSD(T)/6-311+G(3\(d\)\(f\)), and MRCI/TZVPP methods [18], and also of Se\(_n\) structures \((n = 1-5)\) at the DFT level [28, 29] with seven different functionals in the DZP++ basis set [19]. The bond lengths predicted in this work by the DFT/B3P86 method for selenium dioxide are well consistent with the experimental results, while the dissociation energy of OSeO was well reproduced by the BPW91 exchange correlation functional. The authors of [19] note that the adiabatic electron affinity, which they calculated at the theoretical BLYP/DZP++ and BPW91/DZP++ levels, is the most reliable for all selenium oxygen clusters Se\(_n\) \((n = 1-5)\), while the B3LYP functional enabled a good prediction of the vibrational frequencies of selenium oxide.

We have chosen the 6-311++G(2\(d\)) basis set and the B3LYP functional after the pre-calculations of dissociation energies of the O\(_2\) molecule by different methods with different basis sets. The O\(_2\) dissociation energy \((D_e)\) that we calculated by the DFT/UB3LYP/6-311++G(2\(d\)) method is 5.28 eV. With regard to the experimental value of the zero vibrational energy \(\nu(O–O) = 1580\) cm\(^{-1}\) we obtain \(D_e = 5.09\) eV, which is in good agreement with an experimental value of 5.12 eV [30]. In peroxo- Se(O\(_2\)) \((C_3)\) and SeOO \((C_1)\) selenium superoxocomplex, the oxygen molecule partially retains its properties, therefore, in the calculations, it is essential to reproduce the dissociation energy of the O–O bond, O\(_2\) electron affinity, and the