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INTERACTION OF QUINTET OXYGEN $O_2(^5\Pi_g)$ WITH BENZENE IN THE RAREFIED GAS PHASE

The oxygen molecule plays an important role in the biosphere. It participates in the respiratory aerobic processes of life, protects living organisms from harsh solar radiation and is responsible for the processes of combustion and slow oxidation. The details of many chemical and physical phenomena involving the O_2 molecule are associated with the presence of low-energy singlet excited states, a nonzero magnetic moment in the ground triplet state and the metastable quintet state of the oxygen molecule. Electronic transitions between these states in the electric dipole approximation are strictly forbidden by spin, by orbital angular momentum projection, and by parity. Delocalization of the spin density, change of the π electronic structure due to $O_2(^5\Pi_g)$ collision with aromatic molecule has not been studied so far. Such studies may help to understand the mechanism of energy transfer upon interaction between aromatic molecules and metastable O_{2*}. Therefore, we study here the properties of the $O_2(^5\Pi_g)$ + C_6H_6 complex because benzene is an aromatic molecule with a high polarizability. In our paper we present study of the $O_2(^5\Pi_g)$ interaction with benzene molecule using the powerful UB3LYP/6-311++G(d,p) approach of DFT method. We have started from the very big collision distance of 3 Å and performed geometry optimization until we get a tightly bound addition product. This leads us to the formation of two new C-O˙ bonds in the associate of $O_2(^5\Pi_g)$ molecule and benzene without barrier. By using such a simple approach, we were able to purify the configuration state function, which is a complicated multi-electron problem that occurs at the first-principles computational level. Collected results are very

important in estimating the effect of oxygen on the aromaticity and reactivity of benzene and other organic unsaturated substances.

Keywords: quintet oxygen, nightglow, density functional theory, spin density, electric polarization.

1. Introduction

The lowest quintet excited state of the oxygen molecule $O_2(^5\Pi_g)$ is a highly metastable product of the $O(^3P) + O(3P)$ recombination reaction, which occur in the upper atmosphere. At the height of about 80-110 km concentration of the ground state $O(^3P)$ oxygen atoms is comparable with the O_2 concentration, because of efficient photo-dissociation in the Schuman-Rung continuum $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ under the strong UV solar radiation in the Earth's upper mesosphere and lower thermosphere (MLT) region [1–5]. Thus, the permanent atomic recombination in the MLT part of our atmosphere leads to production of all possible O_2 excited states lying below the dissociation limit 5.1 eV. These are well-know $A^3\Sigma_u^+$, A' $^3\Delta u$, $c^1\Sigma_u^-$, $b^1\Sigma_g^+$, $a^3\Delta_g$ excited states; the ground $X^3\Sigma_g^-$ state also can be produced [1, 2]. These states are generated upon tree-body recombination $O(^3P) + O(^3P) +M = O_2* + M$ with equal probability according to their statistical weight; here M is N_2 or O_2 molecules from the low-pressure atmospheric environment. The physically stable $O_2(^5\Pi_g)$ state, which energy lies just below the dissociation limit (at about 5 eV), was discovered quite recently [3–5] and have been included into the kinetics model called "multiple airglow chemistry" (MAC) scheme [1]. In the rarefied gas of MLT region all the excited O_2* molecules can survive during short radiative lifetime, but this is enough to produce energy transfer to the nearby oxygen atom exciting it to the metastable $O(^1S)$ state, which can emit green line at 557 nm in the spin-forbidden $O(^1S \rightarrow {}^3P)$ tranision. This green light was observed by Ångström in the nightglow of atmosphere for the first time one hundred fifty years ago [4]. The notion that nightglow comes to us from the altitude 80–110 km of MLT region and includes also emission of singlet oxygen was realized much later [1–6]. But the role of the $O_2(^5\Pi_g)$ state in these processes is still unknown.

2. Results and discussion

In order to explain the nightglow the MAC scheme comprises a big number of radiative and non-radiative transition rates for various O_2* states and collisions [1,4], but the knowledge about physico-chemical properties of the $O_2(^5\Pi_g)$ quintet molecule are rather limited. The $O_2(^5\Pi_g)$ molecule cannot relax to the low-lying $A^3\Sigma_u^+$, A' $^3\Delta u$, $c^1\Sigma_u^-$, $b^1\Sigma_g^+$ states since there is no spin-orbit coupling (SOC) between these state. The quintet-singlet and "g-u" mixing by SOC is forbidden [7–9]. The only allowed way for relaxation is the $O_2(^5\Pi_g) - O_2(X^3\Sigma_g^-)$ non-radiative channel through interaction by SOC at long intermolecular distance (r). This region is characterized by fast passing upon recombination and such relaxation rout is not efficient. Potential energy curves of these two states show a crossing around internuclear distance r=2.2 Å, which is much larger than the quintet $O_2(^5\Pi_g)$ state equilibrium (Fig. 1) (r=1.913 A) [4]. Thus, the lowest zero vibrational level of the $O_2(^5\Pi_g)$ quintet state has no effective rout of electronic relaxation in free oxygen molecule. Thus, the state $O_2(^5\Pi_g)$ is expected to be metastable; its lifetime is measured to be longer than 2 µs at pressure of 4−9 Torr [4]. Upon collision the spin-selection rules can be violated, but the intramolecular interactions still dominate. In our work [4] we have studied recently the chemical reactivity of the quintet $O_2(^5\Pi_g)$ molecule in terms of density functional theory (DFT) [7]. Chemical reactions with Noble gases, N_2, CO_2, H_2O molecules have been calculated with the spin-unrestricted B3LYP functional and stable complex formation predicted. The most tightly bound $H_2O{\ldots}O_2$ $(^5\Pi_g)$ system exhibits binding energy of 19.6 kJ/mol being twice as much

comparing the strongest Noble complex Xe…O_2 ($^5\Pi_g$) [4]. The tight chemical product was predicted for $O_2(^5\Pi_g)$ reaction with the Mg(^{1}S) atom, which is abandon in the meteoritic clouds in the mesopause MLT range at about 90 km altitude. Huge dissociation energy (D_0 = 266 kJ/mol) of the $^5A_1$ quintet state was obtained for excited MgO_2 molecule [4]. The quintet $^5A_1$ state of this product is much more stable than the ground $^3A_2$ state of magnesium peroxide (D_0 =61 kJ/mol) [4].

About 50 tons of interplanetary meteoritic dust fly into the upper atmosphere of our planet every day. Meteor ablation is responsible for the growth of Mg, Ca metal atoms layers 1–2 km thick, which spread globally at the MLT altitudes. Interaction of quintet $O_2(^5\Pi_g)$ species with Mg atom produces tightly bound $MgO_2(^5A_1)$ molecule, which can survive during 0.6–2.4 μs before relaxation to the ground state. This lifetime is estimated by SOC account (36 cm^{-1}) between $^5A_1$ and $^3A_2$ states with energy gap of 2.83 eV; vibrational modes are calculated at the quintet state optimized geometry. Intersysten crossing rate is rather slow and the lifetime is long enough in order produce important kinetic sequences in the framework of MAC scheme.

These predictions can be tested also in laboratory. Vaporization of solid MgO_2 accompanied by laser (440 nm) excitation with flash photolysis can provide information on the $^5A_1$ state. Our SOC calculation predicts oscillator strength 3.2×10^{-8} for the $^5A_1 \leftarrow {}^3A_2$ transition, which could be observed also in emission with radiative lifetime 0.09 s. The strong interaction of $O_2(^5\Pi_g)$ species with Mg encouraged as to calculate the quintet dioxygen collisions with aromatic organic molecules, which possess high polarizability and interesting photo-physical properties. DFT method permits to calculate quintet state, which corresponds to $O_2(^5\Pi_g)$ interaction with ground state aromatic molecule.
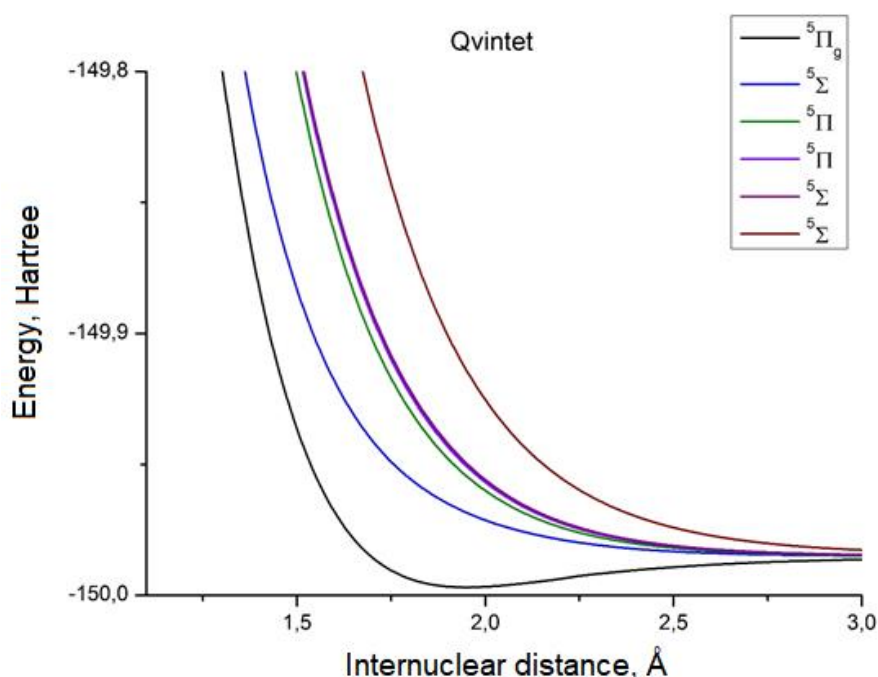

Fig. 1. Potential energy curves of low-lying O_2 quintet states.
Рис. 1. Криві потенціальої енергії низько лежачих квінтетних станів O_2.

Here we present our study of the $O_2(^5\Pi_g)$ interaction with benzene molecule using the same UB3LYP/6-311++G(d,p) approach of DFT method [7]. Starting with collision distance of 3 Å we performed geometry optimization and obtained a tightly bound addition product shown in Fig. 2. The $O_2(^5\Pi_g)$ molecule is attracted by benzene without barrier and dissociates providing two new C-O˙ bonds. Each oxygen atom bears non-paired electron spin and two

non-paired electrons are delocalized in the benzene ring (Fig. 2b). The adduct shows strong electric polarization especially in the low part of the ring (Fig. 2a). This is very unusual species, which release big energy upon $O_2(^5\Pi_g) + C_6H_6$ addition reaction ($D_0 = 59$ kJ/mol). The benzene ring remains to be almost planar (deviation from planarity is 4,4°). The upper part of the ring has shorter C–C bond lengths (1.384 Å), but the middle and lower C-C links (1.502 and 1.496 Å, respectively) are longer than those in the free benzene molecule (1.395 Å). The valence angle H–C–O is equal 99.98° being far from the tetrahedral one (109.45°). Spin density shows quait strong alternation in the benzene ring (Fig. 2). The calculated dipole moment is equal 3.42 D being oriented perpendicular to the ring.
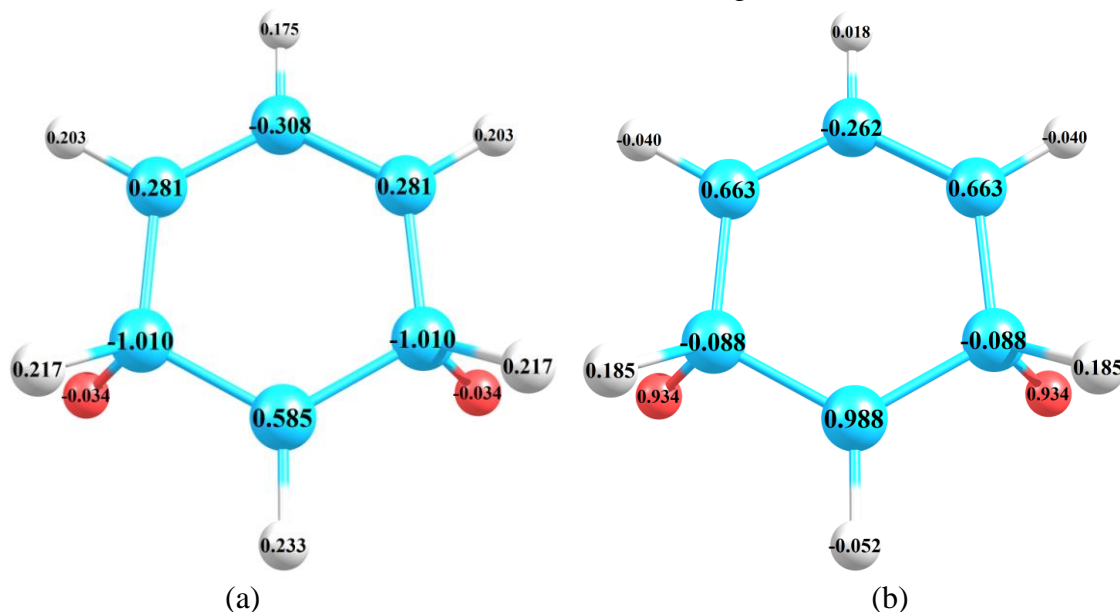

(a)   (b)

Fig. 2. Atomic charges (a) and atomic spin density (b) in the quintet state of the product of the $C_6H_6 + O_2$ ($^5\Pi_g$) addition reaction.

Рис. 2. Атомні заряди (а) та атомна спінова густина (б) у квінтетному стані продукту реакції приєднання $C_6H_6 + O_2$ ($^5\Pi_g$).
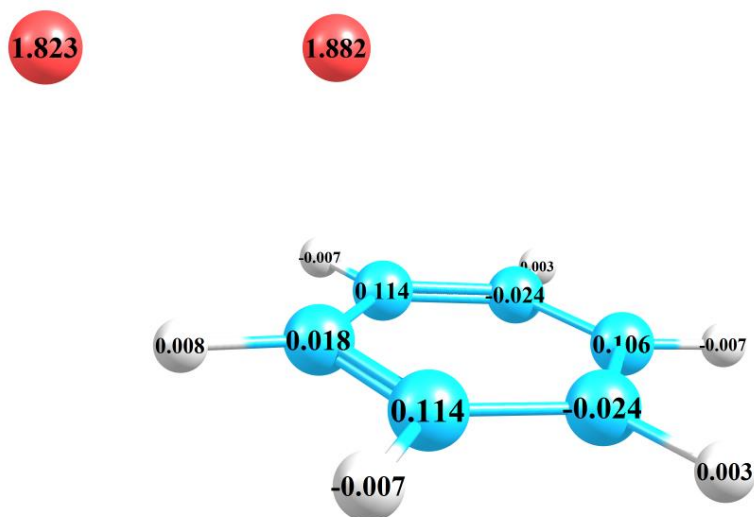

Fig. 3. The most weakly bound collision complex between benzene and the quintet oxygen $O_2(^5\Pi)$ molecule.

Рис. 3. Найбільш слабко зв'язаний комплекс зіткнень між бензолом і квінтетною молекулою кисню $O_2(^5\Pi)$

We also optimized a weak collision complex (Fig. 3) with bonding energy of 5.2 kJ/mol. Dioxygen molecule in this case does not dissociate, but only slightly deformed upon rather weak intermolecular interaction. The distance between nearest C and O atoms is equal 2.35 Å. The terminal O atom has negative charge (–0.15 e), while the "bound" oxygen atom is almost neutral (0.03 e). Electric polarization in benzene ring is rather moderate.

Spin density distribution shows a small spin transfer from dioxygen; only 3.705 instead of 4 non-paired spins resides on O_2 moiety. Aromatic benzene ring withdrows a large part of dioxygen spin density inspite of the weak collision. The largest spin density (0.114) is concentrated on orto-carbons of benzene. The O–O bond is longer (1.93 Å) than in free O_2 ($^5\Pi_g$); this means that aromatic ring produces rather strong perturbation in the highly sensitive O_2 ($^5\Pi_g$) species. All optimized structures show only real vibration frequencies. Calculations are performed with the Gaussian-09 code [7]. The weak complex (Fig. 3) and stable quintet product (Fig. 2) exhibit peculiar properties, which differe from all stidued associates between triplet O_2 ($X^3\Sigma_g^-$) molecule and various organic and inorganic species, including transition metal compounds with high electronic spin [8–22].

3. Conclusions

This study is a preliminary approach to establish the problem of O_2 ($^5\Pi_g$) chemistry at the classical adiabatic level. A spin-unrestricted DFT method was applied for geometric optimization of the lowest singlet state in reaction with C_6H_6. By using such a simple spin fixation, we were able to purify the configuration state function, which is a complicated multi-electron problem that occurs at the first-principles computational level. It was revealed, that the C_6H_6–O_2 ($^5\Pi_g$) complex exhibits both weak stability and strong stability (5.9 kJ/mole and 52 kJ/mole, respectively) by oxygen fixation in different potential wells. This result is very important in estimating the effect of oxygen on the aromaticity and reactivity of benzene and other organic unsaturated substances. In the future, it will be necessary to perform similar calculations for other solvent molecules with account of correlation and relativistic effects.

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ВЗАЄМОДІЯ КВІНТЕТНОГО КИСНЮ $O_2(^5\Pi_g)$ З БЕНЗОЛОМ У ФАЗІ РОЗРІДЖЕННОГО ГАЗУ

Молекула кисню відіграє важливу роль у біосфері. O_2 бере участь у респіраторно-аеробних процесах життя, захищає живі організми від жорсткої сонячної радіації, відповідає за процеси горіння та повільного окислення. Деталі багатьох хімічних і

фізичних явищ за участю молекули O_2 пов'язані з наявністю низько-енергетичних синглетних збуджених станів, відмінного від нуля магнітного моменту в основному триплетному стані та метастабільного квінтетного стану молекули кисню. Електронні переходи між цими станами в наближенні електричного диполя суворо заборонені спіном, проекцією орбітального кутового моменту і парністю. Також досі не вивчена делокалізація зміни густини π-електронів внаслідок зіткнення ароматичних молекул з метастабільним O_2^*. Такі дослідження можуть допомогти зрозуміти механізм переносу енергії при взаємодії між ароматичними молекулами та $O_2(^5\Pi_g)$. Тому ми вивчаємо властивості комплексу $O_2(^5\Pi_g) + C_6H_6$, оскільки бензол є ароматичною молекулою з високою поляризуємістю. У нашій роботі представлено дослідження взаємодії $O_2(^5\Pi_g)$ з молекулою бензолу за допомогою потужного підходу UB3LYP/6-311++G(d,p) за методом DFT. Ми почали з дуже великої відстані зіткнення в 3 Å і проводили оптимізацію геометрії, поки не отримали щільно зв'язаний продукт приєднання. Це призводить до утворення двох нових зв'язків С-О˙ в асоціаті молекули $O_2(^5\Pi_g)$ і бензолу без бар'єру. Використовуючи такий простий підхід, ми змогли очистити функцію стану конфігурації, яка є складною багатоелектронною проблемою, що виникає на обчислювальному рівні першого принципу. Зібрані результати дуже важливі для оцінки впливу кисню на ароматичну та реакційну здатність бензолу та інших органічних ненасичених речовин.

Ключові слова: квінтетний кисень, нічне світіння атмосфери, теорія функціоналу густини, спінова густина, електрична поляризація.