Structure, Energy, and Vibrational Frequencies of Oxygen Allotropes Oₙ (n ≤ 6) in the Covalently Bound and van der Waals Forms: Ab Initio Study at the CCSD(T) Level

Oleg B. Gadzhiev,Stanislav K. Ignatov,Mikhail Yu. Kulikov,Alexey G. Razuvaev,Peter G. Sennikov, and Otto Schrems

1Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, 46 Ulyanov Street, Nizhny Novgorod, 603950, Russia
2G.G. Devyatkykh Institute of Chemistry of High Purity Substances, Russian Academy of Sciences, 49 Troponina St., Nizhny Novgorod, 603950, Russia
3N.I. Lobachevsky State University of Nizhny Novgorod, National Research University, 23 Gagarin Avenue, Nizhny Novgorod, 603950, Russia
4Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

Supporting Information

ABSTRACT: Recent experiments on the UV and electron beam irradiation of solid O₃ reveals a series of IR features near the valence antisymmetric vibration band of O₃ which are frequently interpreted as the formation of unusual O₄ allotropic forms in the forms of weak complexes or covalently bound molecules. In order to elucidate the question of the nature of the irradiation products, the structure, relative energies, and vibrational frequencies of various forms of Oₙ (n = 1–6) in the singlet, triplet, and, in some cases, quintet states were studied using the CCSD(T) method up to the CCSD(T,full)/cc-pVTZ and CCSD(T,FC)/aug-cc-pVTZ levels. The results of calculations demonstrate the existence of stable highly symmetric structures O₄ (D₂d), O₆ (D₃h), and O₈ (D₃h) as well as the intermolecular complexes O₃O₂, O₂O₃, and O₄O₃ in different conformations. The calculations show that the local minimum corresponding to the O₃...O complex is quite shallow and cannot explain the ν₃ band features close to 1040 cm⁻¹, as was proposed previously. For the ozone dimer, a new conformer was found which is more stable than the structure known to date. The effect of the ozone dimer on the registered IR spectra is discussed.

1. INTRODUCTION

The existence of the higher neutral allotropic forms of oxygen Oₙ (n > 3) is an intriguing and fundamental question in inorganic and physical chemistry. The idea about the existence of O₄ dates back to early works of Dolezalek and then Lewis,1,2 to possibly explain the magnetic properties of liquid oxygen. In the end of the 1970s, the influence of the complexes (O₂)₂ on the energy balance in the atmosphere attracted the attention of spectroscopists. In 1980, Adamantides et al.3,4 studied theoretically for the first time the covalently bound allotropic form of tetraoxygen O₄, establishing that the molecule has a cyclic structure of D₃h symmetry. Later, Roggen and Nilssen5 demonstrated that the “pinwheel” D₃h structure of O₄ is also stable, although less energetically favorable than the cyclic isomer. The studies of tetraoxygen were continued in theoretical studies.5–24 Among them, the most fundamental results were obtained by Seidl and Schaefer,7,8 who investigated the thermodynamic and kinetic stability of cyclic O₄ (up to the CCSD(T)/DZP level) including the transition states and activation energies of the O₂ dissociation, and more recently by Hernandez-Lamoneda and Ramirez-Solis,16,17 who obtained high-level data for the O₄ structure and energy using the CCSD(T)/aug-cc-pVQZ and CASSCF(16,12)-ACPF//CASSCF(16,12)-RS2 methods. These values were also confirmed by Caffarel et al.25 who reported the energy of O₄ calculated using the multireference quantum Monte Carlo theory. This theory can potentially account for a greater amount of electronic correlation than the CCSD(T) method. It follows from these works that O₄ can exist in two singlet-state isomeric forms: cyclic puckered D₂d and open planar D₃h structures. The energy of the D₂d structure relatively to O₂ (Σ⁺) is ~93–95 kcal/mol; the energy of the D₃h structure is about 116.2 kcal/mol (value obtained in refs 26 and 27 at the CCSD(T)/TZ2P level). The activation barrier of dissociation of the cyclic structure to 2O₂ is estimated to be in the range of 6.6–9.3 kcal/mol17 or 11.6 ± 1.6 kcal/mol.22 Such remarkable activation barrier height stimulated attempts of experimental detection of covalently bound O₄. The first experimental observation was reported by Bevsek et al.28 who formed O₄ by DC discharge and O₃ photolysis observing the REMPI spectrum assigned to O₄ of the D₂d structure. Later,

Received: July 27, 2012
Published: November 16, 2012
Peterka et al.\textsuperscript{26,27} reported an O$_4$ observation on the basis of the rotationally resolved photoionization spectra, photoelectron spectra (combined with \textit{ab initio} calculations) which were considered “strong evidence of metastable O$_4^*$.\textsuperscript{4}” The last statement was then questioned by Chestakov et al.\textsuperscript{29} who concluded that the spectrum observed in refs 26 and 27 appears due to impurities of iron ions in the experimental setup. The most recent detection of O$_4$ was reported by Cacace et al.\textsuperscript{30} on the basis of a neutralization-recharging beam technique combined with mass spectrometry.

It should also be noted that the van der Waals oxygen dimer (O$_2$)$_2$, which is also termed frequently as O$_4$ or tetraoxygen, was also intensively studied both theoretically and experimentally. It was observed experimentally both in the low-temperature matrix\textsuperscript{31,32} and in the molecular beams.\textsuperscript{33} The most recent theoretical studies of intermolecular complexes (O$_2$)$_2$, (O$_2$)$_3$ and (O$_2$)$_4$ are presented in refs 34–36 where high-level \textit{ab initio} and quantum Monte Carlo methods are applied in the investigations for material sciences. The clusters (O$_2$)$_n$ are of particular importance for the oxygen solid state at extremely high pressure.\textsuperscript{37,38} The giant clusters (O$_2$)$_n$ with several thousands of O$_2$ molecular units are potentially important for future technologies based on a relatively new concept called “chemistry with a hammer.”\textsuperscript{33,34,39,40} A polymeric form of oxygen (θ-O$_4$ phase based on a polymeric chain structural motif) was predicted in ref 41 on the basis of DFT calculations.

Although rather complete and detailed information has now been obtained concerning the existence of tetraoxygen, the covalently bound hexaoxygen O$_6$ molecule is studied to a much lesser extent. For the first time, the covalently bound structure of O$_6$ was considered theoretically by Blahous and Schafer\textsuperscript{42} and later by Xie et al.\textsuperscript{43} in the search of “high energy density materials,” i.e., materials which can be used as prospective fuels, propellants, and explosives. It was shown that O$_6$ molecule has a D$_3d$ “chair” structure similar to cyclohexane. In ref 42, only the SCF/STO-3G, DZ, and DZP structure was reported, augmented by frequency calculations. In ref 43, the geometry parameters, IR frequencies, and Raman intensities were studied for the D$_3d$ structure of O$_6$ using the SCF and MP2 theories in the DZP and T22P bases. In 1990s, attention was given to O$_6$ in the series of works of Gimarc and Zhao,\textsuperscript{44–47} who investigated the question of strain energy of the inorganic cyclic compounds from the point of view of structural chemistry. In these works, the structures and energies of O$_6$ were studied on the MP2/6-31G* level along with the structures of other oxygen cycles O$_n$. Later, the DFT and MP2 theories were applied to O$_6$, O$_6$, O$_6$, and O$_{12}$–.\textsuperscript{48} In that work, the stable structure of O$_6$ (and also O$_6$) was not found at the DFT level (B3LYP and B3PW91 with conjunction 6-31G* and 6–311G(2df) basis sets) but was optimized using the MP2 calculations, although the corresponding energies and structural data were not reported. In the experimental and theoretical study of Probst et al.,\textsuperscript{49} it was also reported that MP2/6-31G* calculations were performed for O$_6$ (and MP2/DZP for O$_6$) without detailed presentation of the calculation data. In 2002, there was a report\textsuperscript{50} that the O$_6$ and O$_6$ ozone clusters were optimized at the PM3 level and using the MP4/6-311++G(d,p) and QCISD/6-311+G(d,p) potential curve calculations. The ozone dimerization energy estimated here was approximately 1 kcal/mol; however, the structure of the ozone dimer was rather different from that obtained earlier by Slanina.\textsuperscript{50,51}

Thus, there is a lack of information concerning the covalently bound hexaoxygen O$_6$. Moreover, the data on the structure, binding energies, and the vibrational frequencies of the ozone van der Waals dimer were obtained a long time ago using a level of theory which is not appropriate for the needs of the present day. Namely, it is not clear whether the structure of the dimer observed in the inert matrix by Schriver et al.\textsuperscript{52} corresponds to the structure considered by Slanina.\textsuperscript{50,51}

In the middle of 1990s, experiments on the UV irradiation of the solid oxygen films conducted in different laboratories raised a question about the possible formation of unusual forms of the oxygen species or complexes in atmospheric ice particles or in space oxygen-rich ice bodies. Namely, in the associated works,\textsuperscript{52,53} the changes in IR spectra of the solid oxygen and oxygen in an argon matrix after UV irradiation were interpreted as a formation of oxides between O$_4$ and atomic oxygen. This fact can have significant effects on the current atmospheric models\textsuperscript{54} and deserve special attention. First, the question is whether the observed results can be interpreted as an O$_4$...O complex. If yes, what are its thermodynamic and spectral properties, spin state, structure, and reactivity? If not, the second question is what species or effects are responsible for the changes in IR spectra observed experimentally? In particular, the question is whether it is possible to describe the observed effects by the formation of oxygen complexes or, probably, other oxygen allotropes.

Therefore, the present work is devoted to the quantum chemical study of the structure, energy, and spectral characteristics of both covalently bound and van der Waals structures of oxygen allotropes O$_{4n}$ ($4 < n < 6$), which can, in principle, be responsible for the observed IR features. Hereafter, we will use the term “bound” for the molecular structures where all the atoms have one or more internuclear distance not longer than 2.5 Å. The species with the elongated contacts (with typical van der Waals O...O distances 3–5 Å) will be referenced hereafter as “molecular complexes.”

The goal of this study is to obtain reliable data on the structure, energy of formation, and vibrational frequencies of polyoxygen in the forms of both a covalently bound molecule and a weakly bound complex in order to make assignments for the infrared bands observed in the solid oxygen irradiation experiments and, thus, a decision on the natures of the species formed during such irradiation. In this case, the frequency calculations and determination IR-shift for the polyoxygen substances at the theory level for the high-correlated method.

In the beginning of the present work, we will make an extensive benchmark of the single reference coupled cluster methodology for the smallest oxygen substances, including the O atoms and O$_2$ and O$_3$ molecules. Next, we will consider the O$_4$ molecules with an extended CAS(24,16) active space. It is the first one which can describe reliably both (cyclic and open) isomers and provide the correct reference functions for the MRCI calculations. The chain form of the tetraoxygen is investigated at the coupled cluster and CASSCF theory levels. Further, we will present results for O$_5$ and O$_6$ molecular units, and later for atomic-molecular and pure molecular complexes calculated at the high-correlated theory levels and verified by the multireference approach.

2. CALCULATION DETAILS

The main computational part was performed at the CCSD and CCSD(T) levels of theory using the cc-pVTZ, aug-cc-pVTZ, and cc-pCVTZ basis sets. cc-pCVTZ is a special kind of basis
set augmented by tight core functions. The importance of core−core and core−valence correlation for high precision calculations was demonstrated in ref 57 (see also refs 58 and 59). As it was shown, the use of the core functions in CCSD(T) calculations remarkably improves the geometry parameters and harmonic frequencies of ozone molecule. We considered this level the most reliable and tried to use it for the geometry optimization and frequency calculation of all the species under consideration. In some cases, however, the calculations on that level were impossible, either because of convergence problems or because the molecule was not stable at this level. In that case, we report the results obtained at lower levels. For the molecular complexes, we also tried to take into account the long-range effects using the basis set augmented by diffuse functions (CCSD(T,FC)/aug-cc-pVTZ).

The CCSD and CASSCF calculations were carried out using the Gaussian 03 program. The Firefly QC package, which is partially based on the GAMESS (US) source code, was used for the preliminary search for stationary points at different levels of the CASSCF method. For the CCSD(T) calculations, the program CFOUR was used, which allows for geometry optimizations with analytic gradients and analytic second derivatives for frequency calculations. Full geometry optimization was performed for all the systems, typically followed by frequency calculations. For the geometry optimizations, several starting points were examined, especially for the flexible structures of molecular complexes. In addition, the MRCl energy calculations were carried out for the O2 molecules and their production from O2. The cyclic O3 was optimized at the strongly contracted NEVPT2/cc-pVTZ theory level with numerical evaluation of gradients. To reduce computational time, the resolution of identity (RI) approximation with an auxiliary cc-pVTZ/C basis set was employed. All the multi-reference calculations beyond CASSCF were carried out with the ORCA suite of programs. For the coupled cluster calculation beyond CCSD(T), the MRCC program interfaced to the CFOUR suite of programs was used. The internal test of the single reference coupled cluster methodology was carried out with the focal point analysis methodology for singlet−triplet splitting of the O atom, the O2 molecule (up to CCSDTQ), and the gap between open and closed O2 (up to CCSDTQ(3)).

For visualization and initial structure preparation, the GaussView03, ChemCraft, and Moltran graphical programs were employed.

3. RESULTS AND DISCUSSION

Atomic Oxygen, Molecular Oxygen, and Ozone.
Electronic structures and physical and chemical properties of the dioxygen substances have been excellently reviewed in ref 78 and more recently. Table 1S (see Supporting Information) presents the calculated energies of atomic oxygen O(1p) and O(1D), as well as the energies, geometry parameters, and harmonic vibrational frequencies of molecular oxygen O2(XΣg+), O2(aΣg+), and O3(X̃A1) at the CCSD/cc-pVTZ level and with the CCSD(T) method in conjunction with basis sets up to aug-cc-pV5Z. These oxygen substances are the reference systems to assess the chosen coupled cluster approach for the polycyanogen species. The results do not override the ones published previously (see Supporting Information for the detailed discussion and Table 1S). However, we employ the data to justify the CCSD(T,FC)/cc-pVQZ and CCSD(T,FC)/aug-cc-pVTZ theory levels chosen here for the main computational study.

Calculated vs Experimental Data. In the presented study, we use the corresponding physicochemical data to verify and justify the high-correlated methods and basis sets applied to the oxygen species. Despite the single reference wave functions used for the description of singlet states of O and O2, the calculated energies and spectral characteristics of the first excited singlet states of atomic and molecular oxygen as well as the geometric parameter (bond length) for O2 show that these states correspond to the multiconfigurational wave functions of O(1D) and O2(aΔg) states, which are triple and double degenerate, respectively, not to O(1S) and O2(bΣg+), as takes place frequently in many single-reference calculations. This is probably due to the effect of CCSD(T) excitations, which take into account the large part of the nondynamic correlation required to form the multiconfigurational states. At the same time, the wave function remains to be a proper CCSD(T) solution, as is evident from the values of T1-diagnosis (<0.02).

As is evident from Table 1S (see Supporting Information), the agreement between the calculated and experimental energies of singlet–triplet transitions of O and O2 species for O(1D)−O(1S) and O2(aΔg)−O2(XΣg+) transitions was typically in the range of 15% (10–15 kj mol⁻¹) at all the theoretical levels and was in better agreement than for O2(bΣg+) ← O2(XΣg+) (error about 100%). Geometry parameters and vibrational frequencies are also satisfactorily represented for O2 both in triplet and singlet electronic states. Typical deviation of the calculated harmonic vibrational frequencies is about 10 cm⁻¹ for the O2(XΣg+) vibrations and 40–50 cm⁻¹ for the O2(aΔg) vibrations. The latest discrepancy has probably some contribution due to the lower accuracy of experimental data on the excited O2(aΔg) state.

The vibrational frequencies of O (719.6, 1062.1, 1157.8 cm⁻¹) and O2 (1580.19 cm⁻¹ for 3Σg− electronic state) calculated at the CCSD(T,full)/cc-pVQZ level are in good agreement with the experimental harmonic frequencies 716.0 cm⁻¹, 1089.2 cm⁻¹, and 1589.15 cm⁻¹ for the O3(X̃A1) open form and O2(Σg+), respectively. It should also be noted that the data calculated at the CCSD(T,full)/cc-pVQZ level are in agreement with CCSD(T,full)/cc-pVTZ and CCSD(T)/aug-cc-pVTZ results. However, inclusion of a tight core function in the basis set improves significantly the calculated data for O3 and O2. At the CCSD(T,full)/cc-pVQZ level, the differences from the experimental parameters for O2 (3Σg− and 1Δg) and O3(X̃A1) are only about 0.001 Å for O–O bond lengths and about 25 cm⁻¹ for the “worst case” of vibrational frequency υ3 (symmetric stretch belonging to 1A1 irreducible representation) of ozone, which is well-known to be difficult to correctly predict.

Watts and Bartlett performed a very extensive survey of coupled cluster methodology up to the CCSDT method. On this basis, we calculated the remaining error from the neglect of relativity and made a direct comparison with experimental data. We calculated the average internuclear distances (r̃g) and the distance between the average nuclear positions (r̃g) with a harmonic force field and cubic force constants calculated at the CCSD(T,FC)/aug-cc-pVQZ theory level. The errors were found to be negligibly small. Details of this analysis are given in the Supporting Information.

Previously, Müller et al. explored the PES of the O2 system using the multireference configuration interaction (MR-CI) method in both internally contracted (ic) and non-contracted
The Cyclic O₃ (D₃h) Molecule. The existence of the cyclic (D₃h) ozone isomer as a metastable structure was proposed by Peyerimhoff and Buentker⁹⁵ on the basis of HF-SCF calculations and was confirmed later using post-HF methods.⁹⁶⁻¹⁰⁰ The results of the coupled cluster calculations at the CCSD(T)/NASA-Ames-ANO theory level confirmed¹⁰¹ this conclusion. It was also supported by PES exploration with the CASSCF method.¹⁰² The origin of the metastability of cyclic O₃ was analyzed by multireference calculations in refs 103⁻¹⁰⁵ and by the rate constant calculations for the reaction O₃(D₃h) → O₂ + O in ref 106.

We calculated the parameters for the D₃h form of O₃ at the CCSD(T,full)/cc-pCVTZ level (see Table 1S). The calculated structural and energetic parameters are in good agreement with the characteristics of this stationary point obtained earlier at other levels of theory⁹⁸⁻¹⁰⁰ including CCSD(T)/aug-cc-pVQZ and the CBS-Q model of Peterson, MRCl, and MR-AQCC with full valence active space CAS(18,12) in conjunction cc-pVCSZ and aug-cc-pVCSZ basis sets.

The performance of the single reference coupled cluster theory for O, O₂, and O₃: Focal Point Analysis. The agreement between the calculated and experimental energies of singlet–triplet transitions of O and O₂ species for O(1D)←O(3P) and O₂(a’Δ)←O₂(X′Σ⁺) transitions was in good agreement with experimental data. However, the observed performance can be caused by a fortuitous compensation of errors for the high-correlated system at the CCSD(T) theory levels. A similar situation can be anticipated for the gap between O₃(D₃h) and O₃(C₆h). The focal point analysis was carried out in the present study for O and O₂ (the latter was optimized at the CCSD(T)/cc-pVTZ level) with energy calculation up to CCSDTQ(fc)/cc-pVTZ and for O₃ (both optimized at the CCSD(T,full)/aug-cc-pVTZ level) with energy calculation up to CCSDT(Q). The data are collected in Table 3S. The total energies for O(3P) and O₂(Σ⁺) calculated here are in agreement with those obtained earlier.¹⁰⁹ A small difference in energies for O₂(Σ⁺) is very likely to be from a small difference in the molecular geometries. For O(1D)←O(3P) and O₂(a’Δ)←O₂(X′Σ⁺) transitions, the values near the full coupled cluster limit are as follows: 196.66 and 99.52 kJ mol⁻¹ at CCSDTQ(fc)/cc-pVTZ, where the estimated errors are not more than 1.08 and 0.28 kJ mol⁻¹. The CCSDT(Q) data are in excellent agreement with the results of the full iterative CCSDTQ approach. The CCSD(T) values (213.63 and 125.4 kJ mol⁻¹) are a reasonably good estimate for the calculated property. For the O atom, the convergence of the coupled cluster expansion is smooth, whereas for the O₂ system the inclusion of quadruple excitations using perturbation theory increased the increment up to a value of 15.05 kJ mol⁻¹, which is higher than the value of the (CCSDT-CCSD(T)) increment. However, after the full iterative treatment by the CCSDTQ method, the result did not change significantly. This observation makes it possible to conclude that the error for the gap (126.35 kJ mol⁻¹) calculated at the CCSDT(Q)/cc-pVTZ level should be lower than the corresponding increment value (6.92 kJ mol⁻¹).

The data given in Table 2S justify the ability of the CCSD(T) method to reproduce properly the main features of oxygen-rich species and reliability of the calculated values (geometrical parameters and harmonic vibrational frequencies) for other species under investigation. Among all the results obtained here, the ones obtained at the CCSD(T,full)/cc-pCVTZ level demonstrate the best agreement for both geometry and vibrational parameters of these molecules among all the CCSD(T) calculations within correlation consistent VTZ-basis sets (Table 1S). We conclude that the combination of the CCSD(T) method with the basis extended by the core functions with explicitly involved core orbitals in the correlated calculations is the most prominent model for the modeling of polyoxygen substances.

Tetraoxygen. For the O₄ molecule, both isomers reported earlier were located on the singlet PES: cyclic D₃d (see Figure 1a) and open (star-like) D₃h (Figure 1b). On the triplet PES, the O₄ molecule does not exist. It was noticed previously⁹ that the cyclic isomer of the O₄ molecule has mainly single reference character of the wave function.

It was supposed earlier on the basis of CAS(6,6), CAS(8,8), and CAS(16,12) calculations that the O₄ system could be described correctly in the CAS(24,16) active space. To our knowledge, such a kind of theory has not been applied to O₄ molecules up to date because it is considered impractical.²⁰

In the present study, we performed the local minima search for both cyc-O₄ and acyl-O₄ at the CAS(24,16)/cc-pVDZ theory level (i.e., full valence active space for the given system) without any symmetry and geometrical constraints followed by the harmonic frequencies calculation. The cyc-O₄ and acyl-O₄ isomers converted to structures characterized by D₃d and D₃h point groups correspondingly (see Figure 1). The vibrational frequency analysis confirmed that both the stationary points are true local minima. Molecule O₄ (D₃h) is more energetically favorable, and the energy of the isomerization reaction O₄ (D₃d) → O₄ (D₃h) is 89.3 kJ mol⁻¹.

The CI vector of the CASSCF(24,16) wave function consists of 1657110 CSFs. The analysis of the configuration interaction (CI) amplitudes for CASSCF(24,16)/cc-pVDZ obtained for both O₄ (D₃h) and O₄ (D₃d) structures shows that the relative weight of the Hartree-Fock configurations (the squared first coefficient of CI expansion vector) is about 0.8. On the basis of this fact and the fact that the structural and energetic parameters calculated at the CCSD(T) and CAS(24,16) levels are close to each other, we conclude that the errors of a single-
reference CCSD(T) approximation do not influence the results significantly.

For the star-like O_4 structure, the CASSCF calculations with extending active spaces up to CAS(16,12) within 6-31G(d), cc-pVVDZ, ANO-DZ, and 6-311G(d) basis sets result in a symmetry breaking structure with a C_{2v} point group that is usually explained by the influence of intruder states. All the attempts to extend the active space by including corresponding quasi-degenerate virtual orbitals and truncate the (24,16) active space by excluding corresponding quasi-degenerate occupied orbitals failed, and no symmetric structures were found.

The low-symmetry chain-like O_4 structure (Figure 2) is a local minimum at the CCSD/cc-pVTZ level. A similar structure was reported earlier. The geometry optimization results in the C_{2h} (zig-zag) structure with an energy of 88.5 kJ mol\(^{-1}\) relative to O_4(\(\Sigma^+_g\)). The structure (Figure 2) remains a local minimum also in the triplet state (with a somewhat elongated intermolecular distance: \(r(O··O) = 1.8481 \text{ Å}\)). However, at higher levels of theory (CCSD(T)/cc-pCVTZ and CCSD(T)/cc-pCVDZ), this structure (both in singlet and triplet states) rearranges to the structures of O_2–O_2 (D_2) or O_3–O (C_{3v}) complexes. The latest one undergoes further rearrangements, as will be described below.

Additional efforts to localize O_4 chain-like structures were applied using a search of local minima at the singlet and triplet PESs of the system at the CAS(16,12)/cc-pVDZ and CAS(24,16)/cc-pVDZ levels. The optimization runs started from a set of structures belong to two point groups C_{2v}, C_{3v} (planar zig-zag), and C_{2} (screw-like). All structures dissociated to the O_2–O_2 complexes (D_2d symmetry group), and no one structure corresponded to the O_4 chain molecule.

Energies, geometry parameters, vibrational frequencies, and IR intensities for both cyclic (D_{2d}) and open (D_{3h}) structures calculated at the CCSD(T)/cc-pVTZ level are given in Table 2 and Table 2S. Like the CASSCF calculations, the cyclic structure O_4 (D_{2d}) calculated at the CCSD(T)/cc-pVTZ level is signi

\[\Delta E = 480.0 \ (466.3) \text{ kJ mol}^{-1} \text{ and } 490.9 \ [483.3] \text{ kJ mol}^{-1}\]

\[\Delta E = 398.7 \ (396.4) \text{ kJ mol}^{-1} \text{ and } 420.6 \ [409.9] \text{ kJ mol}^{-1}\]

\[\Delta E = 229.3 \ (267.8) \text{ kJ mol}^{-1} \text{ and } 287.6 \ [286.5] \text{ kJ mol}^{-1}\]

\[\Delta E = 148.0 \ (197.5) \text{ kJ mol}^{-1} \text{ and } 215.4 \ [213.1] \text{ kJ mol}^{-1}\]

\[\Delta E = -134.3 \ (-120.1) \text{ kJ mol}^{-1}\]

\[\Delta E = -215.7 \ (-189.9) \text{ kJ mol}^{-1}\]

Both O_4 isomers are much higher in energy than molecular oxygen in both the triplet and singlet states. The quasi-isolated O_4(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) monomers were calculated at distances of 10 and 12 Å. In two sets of calculations, the differences between energies of the system at 10 and 12 Å were about 3.7 and 3.2 kJ mol\(^{-1}\) for the MRCI+Q and MRCI-DDCI-3 methods, respectively, revealing the approximate size consistency. The O_4(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) reaction energy calculated at the MRCI+Q and MRCI-DDCI-3 levels based on CAS(16,12) active space are 416.3 and 489.9 kJ mol\(^{-1}\), respectively, with the estimated errors resulting from the incomplete optimization of about 5.7 and 3.2 kJ mol\(^{-1}\). We also obtained significant disagreement in \(E_{gg}\) for the O_4(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) → O_4(\(\Sigma^+_g\)) + O_2(\(\Sigma^+_g\)) reaction calculated with MRCI-DDCI-3 in the active space (16,12) in comparison with those obtained with MRCI-DDCI-3 based on the CAS(24,16)/cc-pVTZ wave function and with MRCI+Q based on CAS(16,12) and CAS(24,16) as well as with the CCSD(T) and CCSDT(Q) methods. This significant discrepancy is not due to a lack of important configurations. This is justified by calculations with reduced selection criteria (\(T_{pre} \text{ and } T_{sl} \)) to \(10^{-7}\) and \(10^{-9}\) au (the resulting \(E\) value is changed by 1.6 kJ mol\(^{-1}\)). This is likely aroused from an imbalanced treatment of electron correlation.
by simplified MR-DDCI-3 wave functions in the truncated model CAS(16,12) active space with respect to MRCI+Q. Hence, we conclude that the MRCI+Q/cc-pVTZ theory level provides a reliable estimate for the $E_f$ in both active spaces, whereas the MR-DDCI-3 method is valid only in the largest active space CAS(24,16).

The $E_f$ values for MRCI methods and obtained at the CCSDT(Q)/cc-pVTZ theory level for cyc-O$_4$ production in both O$_2 +$ O$_2$ and O$_3 +$ O channels are in good agreement with the data calculated previously in ref 22 with the FN-QMC method on the CAS(16,12)SCF wave function; in ref 17 with the CCSD(T), CASPT2 (RS2), and MR-ACFP methods in conjunction with aug-cc-pVQZ basis set; and in refs 7 and 16 at the CAS(16,12)SCF/ANO-DZ and CISD/DZP theory levels. The calculated values for all the formation reaction energies and the O$_4(D_{2d})$–O$_4(D_{sh})$ gap are in strong disagreement with those reported in ref 26: the O$_4(D_{2d})$ and O$_4(D_{sh})$ formation energies and the gap between O$_4$ isomers are as follows: 511.4, 629.1, and 117.7 kJ mol$^{-1}$. The employed$^{26}$ TZ2P basis set with an (11s6p3d)/(5s3p2d) contraction scheme is not enough since it does not provide converged results.

**Performance of the Single Reference Coupled Cluster Theory for O$_4$ (D$_{sh}$) and O$_4$(D$_{2d}$): Focal Point Analysis.** To verify the reliability of the CCSD(T) results for the O$_4(D_{2d})$–O$_4(D_{sh})$ gap calculation, we performed the focal point analysis in the set of calculations up to CCSDT(Q)/cc-pVTZ (Table 4S). The CCSD(T) and CCSD data (80.7 kJ mol$^{-1}$ and 80.3 kJ mol$^{-1}$, respectively) are in excellent agreement between each other; i.e., the corresponding increment is only 0.5 kJ mol$^{-1}$, and in both the MRCI calculated values. The inclusion of the quadruple disconnected clusters decreased the energy gap to 69.9 kJ mol$^{-1}$, while the increment is 10.4 kJ mol$^{-1}$ for the CCSDT(Q)/cc-pVTZ pair. The excellent agreement of the CCSDT(Q)/cc-pVTZ results with those obtained by the MRCI and MRCI-DDCI-3 calculations is very likely to be elucidated by the significant influence of non-dynamic electron correlation, which is only partially covered by the CCSD(T) method, since the nonmonotonous convergence for the coupled cluster expansion (Table 4S) was observed for an energetic difference between the O$_4$ isomers. However, the CCSD(T) method is still competing in comparison with the most advanced CCSDT(Q) and multireference approaches.

**Pentaoxygen.** The cyclic conformation of the O$_3$ molecule (C$_5$ open nonplanar envelope) was found at the CCSD (CCSD/cc-pVDZ and CCSD/cc-pVTZ, see Table 1 and Table 2S) and CASSCF (CAS(20,15) and CAS(10,10) in conjunction with cc-pVZD and cc-pVQZ basis sets) levels in the singlet state 1$A''$. On the triplet PES, the cyclic O$_3$ structure was not located. The optimized geometry is shown in Figure 3. It should be noted that the value of 0.026 for the $T_1$ diagnostic of CCSD shows a remarkable influence of nondynamic electron correlation not completely covered by single and double excitations.

The CAS(20,15)/cc-pVTZ calculation gives a cyclic structure very similar to that obtained at the CCSD/cc-pVTZ level. This C$_5$ structure (nonplanar open envelope) has O--O bond distances of 1.454 Å and valence angles O--O--O of about 100$^\circ$ (see Figure 3).

To the importance of static electron correlation corresponding to the quasi–degenerate orbitals, we performed the stationary point search with the CASSCF method in different active spaces. It was possible to decrease the active space to (10,10) without the intruder states problem in O$_5$ geometry optimization. The structure for the active space (10,10) is characterized by the C$_5$ point group (see Figure 3) and has considerably different bond lengths in comparison with CAS(20,15)/cc-pVTZ (the O$_2$–O$_2$ bond length 1.433 Å and 1.417 for (10,10) and (20,15) active spaces, respectively, and the O$_4$–O$_4$ bond length from 1.538 to 1.505 Å). The O$_2$–O$\delta$ bond length was not affected by the choice of active space (1.454 and 1.457 Å). The relative weights of the Hartree–Fock configurations are about 0.79 and 0.82 for the CAS(20,15) and CAS(10,10) active spaces, respectively.

It is hard to accurately estimate the dissociation energy at the CASSCF level because it is not rigorously size-consistent in the truncated active space. At the CAS(20,15)/cc-pVZD level, it was possible to find the saddle point for homolytic dissociation O$_5$ → O$_3$ + O$_2$ at the CAS(20,15)/cc-pVZD level in the geometry optimization without any constraints (Figure 4).

The transition state is characterized by the C$_5$ point group and the relative weight of the Hartree–Fock configuration by about 0.75. The comparison between the structures of local minimum and transition state shows that the O–O bond length corresponding to eliminated dioxygen O$_2(\Delta g)$ is significantly reduced in TS by about 0.15 Å (from 1.586 Å to 1.435 Å) in contrast with the O–O bond length corresponding to the forming ozone molecule which is only moderately reduced by 0.071 Å (from 1.346 Å to 1.365 Å). The O–O distance between O$_2$ and O$_3$ fragments is increased by about 0.22 Å.

### Table 1. Calculated Energies and Geometry Parameters of the Covalently Bound Forms of O$_3$ and O$_5$ Polymorphs (Vibrational Frequencies and Intensities Given in Supporting Information)$^a$

<table>
<thead>
<tr>
<th>theory level</th>
<th>$\Delta E$</th>
<th>geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>77.2</td>
<td>O$_3$ (singlet $C_5$ cyclic) Figure 3</td>
</tr>
<tr>
<td>CCSD(T,full)/cc-pVTZ</td>
<td>dissociation to O$_2$ + O$_3$ (van der Waals complex)</td>
<td></td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>67.4</td>
<td>O$<em>3$ (singlet $D</em>{3h}$, chair)</td>
</tr>
<tr>
<td>CCSD(T,full)/cc-pVTZ</td>
<td>58.3</td>
<td>O$<em>5$ (singlet $D</em>{3h}$, twist)</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>78.2</td>
<td>O$<em>5$ (singlet $D</em>{3h}$, twist)</td>
</tr>
<tr>
<td>CCSD(T,full)/cc-pVTZ</td>
<td>dissociation with O–O bond cleavage</td>
<td></td>
</tr>
</tbody>
</table>

$^a$For the O$_3$ data, see Supporting Information. $^b$Energy of O$_n$ per atom relative to (1/2)O$_2(\Sigma_g^+)$.

![Figure 3. The structure of O$_5$ optimized at the CCSD(FC)/cc-pVTZ, CAS(10,10)/cc-pVTZ [in square brackets], and CAS(20,15)/cc-pVTZ [in curly brackets] theory levels. Bond lengths are given in Å, bond angles in degrees.](image-url)
The activation energy $E_a$ of the synchronous dissociation ($O_3 \rightarrow O_1 + O_2$) optimized at the CAS(20,15)/cc-pVDZ theory level. Bond lengths are given in Å, bond angles in degrees.

The activation energy $E_a$ of the synchronous dissociation is 8.6 kJ mol$^{-1}$ at the CAS(20,15)/cc-pVDZ level; the energy of the reaction $O_3(1A') \rightarrow O_3(1A_1) + O_3(1A_2)$ is $-41.1$ kJ mol$^{-1}$. This shows that CASSCF in the truncated active space underestimates the energy of the reaction probably because of noneffective treatment of the dynamical electron correlation.

At the CCSD(T)/cc-pVTZ level (Table 1), all the attempts to find the covalently bound structure for the $O_3$ molecule failed despite many different starting structures being used. Geometry optimization at this level proceeds via the longest (1.53 Å) O=O bond cleavage and finishes near floppy complex OO=O=O with the unconverged CCSD procedure, which is evident for the obvious multireference character of the complex. The $T_1$ diagnostic value 0.0268 calculated at the CCSD/cc-pVDZ level at the structure corresponding to the CAS(20,15)/cc-pVDZ local minimum was noticeably higher than 0.02.

The contradiction between CASSCF and CCSD(T) approaches deserves a special consideration. The main Shortcoming of the CCSD(T) method is the loss of accuracy in the presence of electronic orbitals' near degeneracies. However, it is not obvious whether the near degeneracy can cause the failure of the single reference approach in any particular case, e.g., in cyclic $O_5$ because sometimes singlet biradicals (well-known bad-behaved systems) can be described correctly at the CCSD(T) level. Many tests were proposed to analyze this necessity: the $T_1$ diagnostic, its alternative $D_1$ diagnostic, examination of the largest $T_2$ amplitude, and other methods reviewed in ref 115 (see also refs 116 and 117 and references therein).

In our study, the $T_1$ diagnostic and the largest $T_2$ amplitude calculated at the CCSD(fc)/cc-pVDZ theory level at the structure corresponding to the CAS(20,15)/cc-pVTZ local minimum were 0.026 and 0.0728, respectively. Both values and weights of Hartree–Fock configurations indicate that static electron correlation is not negligible; however, the effect is not strongly pronounced. At the same time, the CASSCF calculations have a lack of electron correlation within the CASSCF wave function and have completely no correlation within the core orbitals. The core orbital correlation has a significant effect on the electronic energy. To expose an artifact of CASSCF or CCSD(T) methods for the prediction of $O_3$ molecular structure existence, a stationary point search without any constraint at the full-electron RI-NEVPT2/cc-pVTZ/C theory level with the CAS(10,10) active space with two increments for numerical differentiation (0.005 au and 0.001 au) was performed. For all the optimizations, O=O bond cleavage was observed, although the convergence to any complex was not reached since the active space (10,10) is not size-consistent. The geometry optimization with the approximate size-consistent (20,15) active space is prohibitively time-demanding. Thus, it is believed that the CCSD(T) results are more reliable than both CCSD and CASSCF methods, and there is no bound structure for the $O_3$ complexes except probably extremely weak van der Waals long-distance contact. The cyclic $O_5$ molecule is an artifact of CCSD or CASSCF calculations due to the lack of dynamic electron correlation taken into account.

**Hexaoxygen.** For the covalently bound $O_6$ molecule, the closed structure of the six-membered nonplanar cycle can exist, in principle, in three conformations: $D_{3d}$ ("chair"), $D_{2d}$ ("twist"), and $C_{2v}$ ("boat"). Among them, only two ($D_{3d}$ and $D_{2d}$) were located at the CCSD/cc-pVTZ level (Figure 5).

However, at the higher CCSD(T)/cc-pVTZ theory level, only the $D_{3d}$ conformation was located (Table 1 and Table 2S). Other conformations were rearranging to the different structures (typically to $O_2$ molecules) during the optimization. The $D_{3d}$ conformation is only one structure, being the subject of previous quantum chemical investigations. However, the CCSD(T)/cc-pVTZ level used in the present study is the highest level of theory ever achieved for this substance.

Harmonic frequencies and the corresponding IR intensities calculated at the CCSD(T)/cc-pVTZ level are also presented in Table 2 and Table 2S. It is seen that the covalent bonding results in quite significant changes of the vibrational frequencies. Thus, the spectral features of these molecules isolated in the low-temperature matrices cannot be observed in the region of spectral bands of source $O_3$.

The value of the $T_1$ diagnostic calculated at the CCSD/cc-pVTZ level for corresponding local minima is 0.023, which demonstrates that the nondynamic electron correlation is probably mostly covered by the CCSD(T) method. The CCSD(T) method reproduces correctly also the symmetry and degeneracy of vibration modes for the $D_{3d}$ structures (see Table 2 and Table 2S).

The most surprising property of the located hexaoxygen structure is its quite low relative energy regarding the energy of two separate ozone molecules. The relative energy of the $D_{3d}$ conformation is only 58 kJ mol$^{-1}$ higher relative to free ozone molecules. The low dimerization energy takes place at both the CCSD and CCSD(T) levels. Similar results are obtained also for thermodynamic properties of the compounds calculated in harmonic approximation. The low energy of the $O_6$ ($D_{3d}$) molecule relative to free ozone raises the question of the possibility of experimental observation or synthesis of this structure. On the basis of common physicochemical rules, we can predict that this molecule can be formed from ozone under high pressure conditions.

We carried out the full geometry optimizations at the CAS(16,14)/STO-3G level for both conformers. For the "chair" conformer localized at the CCSD(T)/cc-pVTZ
The CI vector of the CAS(16,14)/STO-3G wave function gives a weight of the Hartree–Fock configuration of about 0.748. This value supports the conclusion about the necessity of inclusion of triple excitations in the coupled-cluster ansatz for qualitative prediction of vibrational spectra. Expanding of the basis set to 6-31G(d) and cc-pVDZ produced distorted molecular structures.

Active space CAS(16,14) for O₃ does not converge correctly to dissociation limit O₆ → 2O₃. We suppose that the full valence active space CAS(24,18) is enough to describe the reaction path because it includes all (quasi)degenerate orbitals, and active space CAS(12,9) shows correct results for the ozone molecule. However, it was impossible to perform the CAS(24,18) calculations for O₆ even with conjunction of the STO-3G basis set because of prohibitive time demands for the active space including 172 320 330 CSFs. Unfortunately, we failed to find any transition state of the dissociation channels. In all the runs, the optimization collapsed to completely erroneous structures with O–O bonds lower than 0.5 Å. This was probably because of the internal instability of the CCSD(T) procedure with many near-degenerate electronic states.

O₂···O Complex. The full optimization of the O₂···O complex in the quintet state (O₂(1Σg)···O(3P)) at the CCSD(T)/aug-cc-pVTZ and CCSD(T(full))/cc-pCVTZ levels results in a linear structure (C₅ᵥ point group) with binding energies of 1.49 and 0.87 kJ mol⁻¹ (124 and 64 cm⁻¹, Table 2), respectively. These values are in good agreement with the previous MRCI+D/aug-cc-pVQZ calculation for the quintet O₃.

<table>
<thead>
<tr>
<th>theory level</th>
<th>$E_{\text{a}}$ [kJ mol⁻¹]</th>
<th>geometry (bond lengths in Å, bond angles in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>-67.0 (rel. O₂(1Σg) + O(3P))</td>
<td>O₂–O (triplet)</td>
</tr>
</tbody>
</table>
| CCSD(T)/aug-cc-cc-
pVTZ | -5.6 (rel. O₂(1Σg) + O(3P)) | O₂–O (singlet) |
| CCSD(T)/cc-pVTZ | -1.5 (rel. O₂(1Σg) + O(3P)) | O₂–O (triplet) |
| CCSD(T)/aug-cc-
pVTZ | -5.2 (rel. O₂(1Σg) + O(3P)) | O₂–O (singlet) |
| CCSD(T)/aug-cc-
pVTZ | -0.9 (rel. O₂(1Σg) + O(3P)) | O₂–O (singlet) |

Table 2. Calculated Energies and Geometry Parameters for the Atomic-Molecular van der Waals Complexes of Oₙ (n = 3 and 4)

The CI vector of the CAS(16,14)/STO-3G wave function gives a weight of the Hartree–Fock configuration of about 0.748. This value supports the conclusion about the necessity of inclusion of triple excitations in the coupled-cluster ansatz for qualitative prediction of vibrational spectra. Expanding of the basis set to 6-31G(d) and cc-pVDZ produced distorted molecular structures.

Active space CAS(16,14) for O₃ does not converge correctly to dissociation limit O₆ → 2O₃. We suppose that the full valence active space CAS(24,18) is enough to describe the reaction path because it includes all (quasi)degenerate orbitals, and active space CAS(12,9) shows correct results for the ozone molecule. However, it was impossible to perform the CAS(24,18) calculations for O₆ even with conjunction of the STO-3G basis set because of prohibitive time demands for the active space including 172 320 330 CSFs. Unfortunately, we failed to find any transition state of the dissociation channels. In all the runs, the optimization collapsed to completely erroneous structures with O–O bonds lower than 0.5 Å. This was probably because of the internal instability of the CCSD(T) procedure with many near-degenerate electronic states.

O₂···O Complex. The full optimization of the O₂···O complex in the quintet state (O₂(1Σg)···O(3P)) at the CCSD(T)/aug-cc-pVTZ and CCSD(T(full))/cc-pCVTZ levels results in a linear structure (C₅ᵥ point group) with binding energies of 1.49 and 0.87 kJ mol⁻¹ (124 and 64 cm⁻¹, Table 2), respectively. These values are in good agreement with the previous MRCI+D/aug-cc-pVQZ calculation for the quintet O₃.

PES cuts along fixed geometry points. The value found there was about 100 cm⁻¹, although the structures were not collinear.

It should be specially noted that the optimization of O₂···O is successful only after a thorough preliminary search of suitable starting orbital occupations, which was performed with the OCCUPATION keyword in the CFOUR suite of programs. The standard orbital occupations based on the Aufbau principle results in no CCSD convergence. As a rule, the same situation takes place also for other weak complexes described below.

In the triplet state, the optimized structures at the CCSD/cc-pVTZ and CCSD(T(full))/cc-pCVTZ levels have significantly higher absolute energies than for the quintet state. It seems that the CCSD procedure converges to the metastable excited states of the O₃ molecule with an energy of about 48 kJ mol⁻¹ relative to the source O₂(1Σg) + O(3P) system. All the attempts to optimize the O₂···O complex in the singlet state at the CCSD and CCSD(T) levels failed. During the optimization, the activationless rearrangement to the O₃ molecule was occurring, which typically finished with the unconverged CCSD procedure. In both quintet and triplet spin states, the complex has only a typical oxygen band near 1600 cm⁻¹, only slightly distorted by the intermolecular interaction. No new bands in the region of 1000–1200 cm⁻¹ which are typical for the free or distorted ozone molecule in the ground state were observed.

For all the local minima optimized for the O₂···O complex, the zero-point vibration energy calculated in harmonic approximation is much higher than the binding energy of the complex (typically about 10 kJ mol⁻¹ for ZPE in comparison with 0.5–1.5 kJ mol⁻¹ for $E_b$ (Table 2)). Thus, even accounting for the approximate character of the ZPE estimation, it is quite doubtful that the complex can exist as a structurally stable compound.

O₂–O Complex. The question of the existence of the complex between ozone and the ground state of the atomic

Figure 6. The structure of the “chair” conformer O₆ optimized at the CAS(16,14)/STO-3G theory level. Bond lengths are given in Å, bond angles in degrees.
oxygen O(3P) arose as a possible explanation of the experimental results obtained in the experiments on the UV (210–250 nm) irradiation of solid oxygen at temperatures of 10–30 K. Initially, Schriver-Mazoulli et al.52 found that UV irradiation with a xenon lamp results in the formation of low-intensity features at 1033 and 1036 cm⁻¹ near the υ3 band of ozone. Later, Dyer et al.53 reported the formation of a strong stable band structure after irradiation of the solid oxygen with a UV laser at 210–260 nm. The new series of intense bands (comparable to the very intense υ3 band of ozone) were observed in region 1029–1038 cm⁻¹. In both cases, the new bands were stable over rather long time intervals and slowly disappeared during annealing to 30 K. The new bands were interpreted as a formation of the complex O3···O(3P). These results were then repeated at a slower resolution to describe the ozone formation from the solid oxygen in the cosmic space.120,121 In both experimental works, the shoulders of the ozone υ3 low-frequency band wings were registered after irradiation. The wings were stable over several minutes after irradiation and were interpreted as a formation of the O3···O complex.

At the same time, the calculations of the O(3P) + O3 PES performed at the CAS(16,12) + CASMP2/ANO-TZ level did not show any remarkable minimum corresponding to this complex at the S0, T0 and T1 PESs (first two correspond to O2(Σg) + O2(Σg) and the third one corresponds to O2(Σg) + O2(Δu) asymptotic). Later Varandas and Llanio-Trujillo20 in the CASSCF and MRCI calculations with different active spaces for the CASSCF reference wave function of the O3 + O system at the triplet (3A) PES, found two TSs for the O3 + O → O2 + O2 reaction with the CASSCF(8,8) method, with an additional intermediate between them. However, the geometry of the intermediate was not reported. This local minimum disappeared at the CAS(8,8)-MRCI/6-311(2d,f) level at the same basis set (with single remaining TS). Thus, controversies exist concerning the existence of the O3···O complex at the triplet PES of the ozone–atomic oxygen PES. It should also be noted that a similar situation takes place for the existence of the complex O3···O at the PES calculated at very comprehensive levels of theory.122,123 The comparison of the kinetic constants was calculated using very accurate PESs (which have a local minimum corresponding to the O3···O complex) does imperfectly agree with the available experimental data, whereas the artificial removal of the local minimum from the PES gives perfect agreement with experimental values.103,119

In order to elucidate the existence of the complex, we performed a study of the O3···O system at different levels of CCSD(T) theory in different spin states. As before, a thorough search of suitable starting occupations was performed before the optimization. While the search of correct electron population was performed (see Table 6S for the determined OCCUPLATION values), it was taken into account that the intermolecular distances in the complex are quite long (3.2–3.7 Å). It is believed that the interaction has mostly van der Waals character, and the interaction of O(3P) and O(1D) atoms with ozone molecules should be approximately equal in energy. At first, the full optimizations were performed at the CAS(16,12)/cc-pVDZ and CAS(24,16)/cc-pVDZ levels for different structures of the O3···O complex in singlet and triplet spin states (see Table 2 and Table 6S). Next for the symmetrical structures we retained the found point groups in the coupled cluster calculations.

The singlet state complexes (O3···O and O2O···O) were additionally optimized with lower geometry restrictions to obtain the planar and nonplanar structures of C1 symmetry at the CCSD(T)/cc-pCVTZ and CCSD(T)/aug-cc-pVTZ theory levels. Among the nonplanar singlet structures, the C1 conformation was located at both the CCSD(T)/aug-cc-pVTZ and CCSD(T,full)/cc-pCVTZ levels (Figure 7). However, the first one has an imaginary frequency (98i cm⁻¹), and the second one has a frequency of 1811 cm⁻¹, which is obviously an artifact that arose because of Hessian instability. Thus, the stability (Table 2) of this structure is questionable.

After the symmetry and geometry restrictions were completely eliminated, the optimization of the complex rearranged quickly to the asymmetric O···O···O structure and then started to rearrange to two oxygen molecules (singlet state). Simultaneously, the CCSD(T) wave function quickly collapsed to an improper solution with a high value of the largest T3 amplitude of 0.06–0.09, and then the calculations were usually breaking due to the bad convergence of CCSD. This rearrangement is in agreement with the CAS(16,12)/cc-pVDZ optimization.

In the triplet state, three different C1 local minima distinguished by arrangement of the ozone O atoms bounded to O were found at the CCSD/cc-pVTZ (Figure 8a) and CCSD(T)/aug-cc-pVTZ levels (Figure 8b,c). At the CCSD(T)/aug-cc-pVTZ theory level, the most stable conformation is the quasi-cyclic nonplanar structure with the O atom bonded to two terminal atoms of ozone. The binding energy (Table 2) of this conformation is valuable (5.2 kJ mol⁻¹) in comparison with the thermal energy at the solid oxygen temperatures (kT = 0.4 kJ mol⁻¹); however, it is significantly less than the harmonic ZPE value for this structure (18.2 kJ mol⁻¹). The second structure (Figure 8c) is much less favorable; its binding energy is only 0.9 kJ mol⁻¹. In this conformation, the O atom is bound to the central atom of ozone. It should be noted that the frequencies calculated at the same level of theory result in an IR shift of the ozone υ3 frequency of −53 cm⁻¹ for the first structure and +48 cm⁻¹ for the second one. Thus, the shifted υ3 bands do not correspond to any experimentally registered features. However, such large IR shifts in the case of the extremely weakly bound complex cause concern that the results can be affected by the Hessian instability due to the influence of the numerous almost-degenerate orbitals or because artificial permutations of orbitals performed to achieve the convergence of the CCSD procedure.

On the basis of these results, we conclude that the O3···O complex has a quite instable character. At the best level of
theory, the binding energy is much less than the ZPE energy. At the same time, the energies of the reactions with the formation of two dioxygenes estimated at the CCSD(T)/cc-pCVTZ and CCSDT(Q,fc)/cc-pVTZ levels are

\[
\text{O}_3 + \text{O}^{(1D)} \rightarrow 2\text{O}_2 \quad \Delta H \approx -360.7 \text{~kJ~mol}^{-1}
\]

\[
\text{O}_3 + \text{O}^{(3P)} \rightarrow 2\text{O}_2 \quad \Delta H \approx -397.5 \text{~kJ~mol}^{-1}
\]

The CASSCF method does not treat efficiently the dynamic electron correlation in the restricted model active space, which is possible to employ for this system. Thus, the binding energy will be significantly overestimated. However, the main properties of the solutions (structures and symmetry point group) can be investigated in order to verify the CCSD(T) results or to guide the subsequent time-demanding geometry optimization with the CCSD(T) method. All the structures depicted in Figure 8 were located on the singlet and triplet PESs in the CAS(16,12)/cc-pVDZ calculations. Hence, while the CCSD(T) optimizations converged, the calculated results are verified and can be used for the determination of the \(\text{O}_3\) complexes' production and comparison of theoretical and experimental IR shifts. While the structure obtained with the CASSCF calculation does not exist in a stationary point search with CCSD(T)/cc-pVTZ and especially CCSD(T)/aug-cc-pVTZ (more reliable for van der Waals complexes localization), it is very likely to be a result of insufficient treatment of the dynamic electron correlation and therefore an artificial localization of the complex.

As was demonstrated by the calculations, the first reaction has low activation energy (the optimization tended to two \(\text{O}_2\) fragments as described above). There are no serious doubts that the second reaction which is also spin-allowed with higher reaction energy has no remarkable barrier of rearrangement. Thus, such a complex cannot stay stable during the long interval of time and should quickly disappear after even slight annealing. Thus, in our opinion, the assignment made on the basis of UV irradiation experiments in refs 52, 53, 120, and 121 should be considered with caution. In our opinion, the possible causes of the intense bands in the 1037–1029 cm\(^{-1}\) region after irradiation could be a result of the formation of ozone monomer molecules or ozone dimers in the matrix environment strongly distorted by the photochemical reactions of oxygen dissociation.

There are some additional indirect arguments supporting this point of view. First of all, as was described above, the high-level calculations of the \(\text{O}_2\) triplet PES give the local minimum for the \(\text{O}_2\) complex (probably metastable, i.e., with the TS of rearrangement to \(\text{O}_3\) lying lower than the energy of isolated reagents), which has a binding energy of about 200 cm\(^{-1}\) (0.6 kcal/mol) and an activation barrier of dissociation in the range of 0–200 cm\(^{-1}\). Thus, the activation energy of removal of \(\text{O}(3P)\) in the solid oxygen matrix (in an environment where \(\text{O}_2\)–\(\text{O}\) contacts are abundant) cannot be significantly higher even if the \(\text{O}(3P)\) atom forms complexes with \(\text{O}_2\).

Anyway, to our knowledge, the structure and the properties of \(\text{O}_3\) reported here are a first consideration of this complex performed at the theoretical level providing qualitative correspondence between the calculated and observed properties of ozone and its van der Waals complexes.

**Oxygen Dimer.** There are abundant studies about the existence of \(\text{O}_2\) dimers, both experimental\(^{33,124,125}\) and theoretical (see, e.g., review book chapter\(^{126}\)) because of the significance of these systems for the chemistry of the atmosphere\(^{127}\) and chemical lasers.\(^{128,129}\) Dioxygen dimers \(\text{O}_2\) still remain a great challenge for quantum chemistry because of an intermolecular type of bonding and different spin couplings which require multi-reference and high correlated wave functions for quantum chemical description of the electronic structure. For descriptions of the energies and spectral characteristics of all the conformations, the good approximations were applied for both ground and excited states in ref 130 where the CASPT2 method with active space CAS\(^{(16,12)}\) in conjunction with the ANO-TZ basis set and the inclusion of a spin–orbital interaction by means of CAS\(^{(12,8)}\) active space and ANO-DZ basis set; in ref 131 where SA-CAS\(^{(4,4)}\)PT2 and SA-CAS\(^{(4,4)}\)SCF with van der Waals correction by \textit{ab initio} results; and in ref 132 where CASPT2, MRCI, ACPF, and composite CCSD(T)/MRCI approaches were applied. The most extensive survey of different electronic states is ref 133. However, it was performed at a moderate theory level CAS\(^{(4,4)}\)Cl/6-311G\((d)\) and only for the H-shaped conformer. Recently, the potential energy curves for all of the proposed conformers of the dimer in 13 electronic states were revised in refs 34 and 40.

In contrast to singlet and triplet spin states, the quintet spin state of the complex \(\text{O}_2\) can be described by high-correlated \textit{ab initio} methods which are the most reliable and exceed significantly the CASPT2 approach for the treatment of intermolecular interactions in weakly bound systems if nondynamical electron correlation is not significant. The PES of the \(\text{O}_2\) dimer was explored with energy calculation using the CCSD(T) method with systematic extension of the ANO–TZ basis set\(^{132}\) and with the aug-cc-pVQZ basis set and extended manifold of the grid points to reconstruct the PES.\(^{134}\)

It was reported earlier, that the oxygen dimer exists in several conformations (T-shaped, X-shaped, linear, and cyclic) and different spin states. However, it was found in the present study that the rectangular conformation is unlikely. All the attempts to optimize it at the CCSD(T) levels resulted either in twisting...
to the twisted (partly X-shaped) D_{2d} conformation or in the rhomboid D_{2} structure. If the rectangular structure was achieved, it typically had imaginary vibrational modes tending to twist the conformation. The only local minima for the rectangular conformation (both triplet and singlet) were found at the CCSD/cc-pVTZ levels. The obtained results show that the oxygen dimers in the quintet state form weak van der Waals complexes with typical binding energies of about 1.3–1.7 kJ mol^{-1}, which is in good agreement with the experimental estimates 1.65 ± 0.08 kJ mol^{-1} in ref 124. The similar values of the binding energy take place in the case of the triplet spin state. The energies and vibrational frequencies of all the located conformations of the O2 dimer are given in Table 3 and Table SS; the structures are shown in Figure 9.

The calculation shows the frequencies of all the conformations are typically slightly distorted frequencies of dioxygen molecules, as expected for the weak molecular complexes. Thus, it is impossible that the dioxygen dimers’ vibrations contribute in any remarkable way to the infrared shifts observed due to oxygen irradiation (observed in the region of ozone bands).

**Complex O_{2}·O_{2}.** In contrast with the structures discussed above, the complex O_{1}···O_{2} was not described earlier, and it is considered for the first time. However, its vibrational frequencies should be close to the observed O3 frequencies because of small perturbation of the O_{1}(1A_{1}) molecule by the singlet (3Δ_{g}) and triplet (3Σ_{u}−) dioxygen.

The CAS(20,15)/cc-pVDZ theory level was chosen for a preliminary search because of the proven size-consistency of this active space, which corresponds to the CAS(12,9) active space for active O and CAS(8,6) for O2. Five different structures were examined as the starting points. The optimized structures are characterized by the C_{s} point group in singlet (1A') and triplet (3A') spin states and are shown in Figure 10. For O_{1}···O_{2} (1A'), the Hartree–Fock configuration is not leading whereas for the O_{1}···O_{2} (3A') its weight is about 0.77. Thus, the probable significant influence of the nondynamic correlation effect can be anticipated from the CASSCF calculations for both spin states of the quasi-cyclic O_{1}···O_{2} complex (see Table 4).

Optimized at the CAS(20,15)/cc-pVDZ level, quasi-cyclic structures were initially for optimizations at different levels with energy calculations using the coupled cluster method. For the singlet (1A') state, the quasi-cyclic stationary points were located at the CCSD(T)/cc-pCVTZ and CCSD(T)/aug-cc-pVTZ levels (Figure 10). However, by harmonic vibrational frequency analysis it was not confirmed that the C_{s}-symmetric van der Waals complex of ozone and dioxygen corresponds to local minima. In this case, there is a small C_{s} symmetry breaking imaginary frequency (26.8i and 42.6i cm^{-1}) at the CCSD(T)/cc-pCVTZ and CCSD(T)/aug-cc-pVTZ levels of theory. This imaginary mode corresponds to the twisting of dioxygen relative to ozone. However, during the reoptimization along this symmetry-breaking mode, no asymmetrical conformations were located because the optimization restored the symmetrical structure.

The calculated shifts of ν_{n}, ν_{n}, and υ_{1} for the O_{1} fragment are 1.2, ~3.7, and 0.6 and 0.9, ~6.6, and 0.2 cm^{-1} for CCSD(T)/cc-pCVTZ and CCSD(T)/aug-cc-pVTZ, respectively.

**Table 3. Calculated Energies and Geometry Parameters for the Intermolecular van der Waals Complexes of O_{3} (n = 4)**

<table>
<thead>
<tr>
<th>theory level</th>
<th>E_{b}^{a} [kJ mol^{-1}]</th>
<th>geometry (bond lengths in Å, angles in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_{2})<em>{3} (quintet D</em>{3h}, twisted)</td>
<td>−1.3 (rel. 2O_{2}(3Σ_{u}^{+}))</td>
<td>r(O−O) = 1.2010 Å, r(O−O) = 3.4102 Å, α(O−O−O) = 79.75°, θ(O−O−O−O) = 88.79°</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>−2.1 (rel. 2O_{2}(3Σ_{u}^{+}))</td>
<td>r(O−O) = 1.2132 Å, r(O−O) = 3.3211Å, α(O−O−O) = 78.95°, θ(O−O−O−O) = 90.2°</td>
</tr>
<tr>
<td>CCSD(T)/cc-pVTZ</td>
<td>−1.6 (rel. 2O_{2}(3Σ_{u}^{+}))</td>
<td>r(O−O) = 1.2100 Å, r(O−O) = 3.3545 Å, α(O−O−O) = 79.6°, θ(O−O−O−O) = 88.1°</td>
</tr>
<tr>
<td>(O_{2})<em>{3} (singlet D</em>{3h} optimization started from rectangular conformation)</td>
<td>−1.3 (rel. 2O_{2}(3Σ_{u}^{+}))</td>
<td>r(O−O) = 1.2010 Å, r(O−O) = 3.4102 Å, α(O−O−O) = 79.75°, θ(O−O−O−O) = 88.79°</td>
</tr>
</tbody>
</table>

Which resulted in the lack of correlation with separated O_{2} (3Σ_{u}^{+}) and O_{1}(1A_{1}) caused, for the first case, symmetry breaking of the complex O_{1}···O_{2} (3A') characterized by the C_{s} point group optimized at the CAS(20,15)/cc-pVDZ level and, for the second case, an impossibility of localizing the intermolecular complex O_{1}···O_{2} which exists obviously from a physical point of view that was confirmed rigorously at the CAS(20,15)/cc-pVDZ theory level.

**Ozone Dimer (O_{3})_{2}** The optimization of the molecular complex of ozone on the CCSD(T)/aug-cc-pVTZ and CCSD(T)/cc-pCVTZ levels results in two structures corresponding to the van der Waals dimer. The first conformation is an open structure of C_{s} symmetry. This corresponds completely to the structure found earlier by Slanina and Adamowicz (T-
shaped conformation). The geometry of the complex is shown in Figure 11. The energy of the conformation is about 8.0 kJ mol\(^{-1}\) at the CCSD(T)/cc-pCVTZ level (7.1 kJ mol\(^{-1}\) at CCSD(T)/aug-cc-pVTZ, see Table 4).

Another located conformation is the closed (six-membered quasi-cyclic) structure of C\(_{2h}\) symmetry with two O···O contacts of 2.8 Å. Up to date, there were no reports on the structure of this shape. At the CCSD(T) level of theory, this structure is more stable than the T-shaped conformation both in the cc-pCVTZ and aug-cc-pVTZ bases, the calculated binding energies are 8.4 and 9.2 kJ mol\(^{-1}\), respectively.

The harmonic frequencies of the T-shaped conformation calculated at the CCSD(T)/cc-pCVTZ level show that the complex is characterized by two positive infrared shifts of the \(\omega_3\) harmonic frequency of ozone: +2 and +4 cm\(^{-1}\). Earlier,\(^{135}\) it was reported that the ozone dimer in argon, nitrogen, and oxygen matrices is characterized by two doublets close to the \(\nu_3\) ozone band, which were interpreted as the bands of ozone dimer in two different matrix sites with shifts of about +2 and −4 cm\(^{-1}\). However, on the basis of the present results, it seems that another assignment is more suitable—two different sites with the positive (+2, +4) and negative (−2, −4) shifts.

The calculation of the IR frequencies for the quasi-cyclic conformation gives two bands near the \(\nu_3\) ozone band. The IR shifts of these bands are (IR intensities in km mol\(^{-1}\)) are given in parentheses) −28.2 (0) and 16.9(182) cm\(^{-1}\) at CCSD(T,full)/cc-pCVTZ and −34.1(0) and 17.9(210) cm\(^{-1}\) at CCSD(T,FC)/aug-cc-pVTZ. However, only one of these bands with positive IR shifts has significant IR intensity.

On the basis of these data, we conclude that the only possible assignment for the experimentally observed bands is the T-shaped conformation in the two different sites of the low-temperature matrix. Although the quasi-cyclic structure is somewhat more favorable in the gas phase, it is unfavorable in the matrix probably because the structure of this conformation is not suitable for the structure of the matrix environment.

**CONCLUSIONS**

In the current work, we performed a comparative study for the structures, energies, and (if applicable) vibrational frequencies of the species O\(_n\) (\(n = 1–6\)) with emphasis on the structural, energetic, and IR-spectral properties of the molecules which can be potentially formed during the irradiation of solid oxygen by UV and electron beams and can give the IR bands in the region of ozone \(\nu_3\) vibration. The goal was to elucidate the question of whether it is possible to explain the observed spectral features in the region of the ozone IR band that arose after irradiation on the basis of higher oxygen allotropes or molecular complexes. Because of the different composition of the species, we used the CCSD(T,full)/cc-pCVTZ and CCSD(T,FC)/aug-cc-pVTZ levels of theory, instead of multi-reference CI or CCSD approaches, which are not practical for the full geometry optimizations, conformational analysis, and IR-spectra simulation in the case of \(n > 4\). However, the chosen theory levels are verified by the focal point analysis method with energy calculations up to CCSDTQ(fc)/cc-pVTZ for O(\(^1\)D), O(\(^3\)P), O\(_2\) (\(^3\)Σ\(^-\)) and O\(_2\) (\(^2\)Σ\(^-\)) and up to CCSDTQ-
Table 4. Calculated Energies and Geometry Parameters for the van der Waals Complexes of Oₙ (n = 5 and 6)

<table>
<thead>
<tr>
<th>theory level</th>
<th>Eₜh [kJ mol⁻¹]</th>
<th>geometry (bond lengths in Å, angles in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>1.1 (rel. O₃(Σ⁺) + O₂)</td>
<td>see Figure 10a</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>1.0 (rel. O₃(Σ⁺) + O₂)</td>
<td>see Figure 10b</td>
</tr>
<tr>
<td>CCSD(T,full)/cc-pCVTZ</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>CAS(20,15)/cc-pVDZ</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>2.2 (rel. O₃(Π) + O₂)</td>
<td>see Figure 10c</td>
</tr>
<tr>
<td>CCSD(T,full)/cc-pCVTZ</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>CAS(20,15)/cc-pVDZ</td>
<td>b</td>
<td>see Figure 10e</td>
</tr>
<tr>
<td>CCSD/cc-pVTZ</td>
<td>6.5 (rel. 2O₃)</td>
<td>see Figure 11a</td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pVTZ</td>
<td>7.0 (rel. 2O₃)</td>
<td>see Figure 11b</td>
</tr>
<tr>
<td>CAS(20,15)/cc-pVDZ</td>
<td>7.3 (rel. 2O₃)</td>
<td>see Figure 11a</td>
</tr>
<tr>
<td>CAS(20,15)/cc-pVDZ</td>
<td>8.3 (rel. 2O₃)</td>
<td>see Figure 11b</td>
</tr>
</tbody>
</table>

*a* Binding energy of the complex relative to the separate monomers. *b* Overestimated at this theory level. *c* Structure does not exist at this theory level.

Figure 11. The structures of the complexes O₃···Oₙ Cₚ (a) and O₃···Oₙ Cₚ (b) optimized at the CCSD(FC)/cc-pVTZ, CCSD(T,FC)/aug-cc-pVTZ (in parentheses), and CCSD(T,full)/cc-pCVTZ (in curly brackets) levels. Bond lengths are given in Å, bond angles in degrees.

For O₃ (D₃h) and O₄ (D₃h), formation and isomerization energies were calculated at the highest ever achieved level, CCSDT(Q)/cc-pVTZ. All the computational results for the single reference method were verified with the MRCI+Q, and MRCI-DDCI-3 multireference methods in conjunction with cc-pVTZ basis set. The best estimates for the CCSDTQ and CCSDT(Q) are found to be in good agreement with the multireference data. On the basis of the overall comparison of experimental data and calculated results, we conclude that the CCSD(T) computational levels provide adequate results competing with the best obtained, whereas the most affordable CCSD/cc-pVTZ level is not a sufficiently highly correlated theory level for most of the studied systems.

Among the calculated structures, a new (cyclic) conformation was found for the (O₃)₂ complex. The local minima of the molecules O₉ and O₆ and the intermolecular complexes (O₃)₂, (O₁)₂, O₃···O₆, and O₉···O₆ were found for the first time using the CCSD and CCSD(T) quantum chemical methods up to the CCSD(T,full)/cc-pCVTZ and CCSD(T,FC)/aug-cc-pVTZ levels as well as at the CAS(16,12)/cc-pVDZ and CAS(24,16)/cc-pVTZ levels. The calculations demonstrate the existence of stable highly symmetric structures O₉(D₃h), O₉(D₃h), and O₆(D₃h) in a singlet state as well as the complexes O···O₂, O₆···O₆, and (O₃)₂ in different conformations. Simultaneously, the existence of the complex O₉···O proposed earlier in the matrix isolation studies is not supported by the CCSD(T) calculations. The harmonic vibration frequencies of the ozone dimer for the located stationary points are in agreement with the IR spectra observed in the argon, solid nitrogen, and solid oxygen matrices. The CCSD(T) calculations performed here for the first time show that covalently bound O₉ in singlet and triplet states does not exist, which is in agreement with numerical optimization at the RI-NEVPT2/cc-pVTZ/cc-pVTZ/C level in active space (10,10). O₉(D₃h), O₉, and O₆ cannot give IR bands in the region of the ñₙ ozone bands (independently of the conformations), as well as the complex O···O₉. The ñO₉ complex in the singlet state does not exist at the CCSD(T)/cc-pCVTZ and CCSD(T,FC)/aug-cc-pVTZ levels, although the two conformations with binding energies of 5.4 and 0.9 kJ mol⁻¹ were found for the triplet state. The frequencies of the located structures are poorly described within the CCSD(T) approach and require applications of more rigorous multi-reference methods. However, this structure cannot be so stable that it gives significant contributions to the long-living intense bands observed in solid oxygen. The most probable candidates for the assignments of the observed spectral features are the ozone dimeric complexes and/or monomeric ozone placed in a different environment (trapping sites) of the solid oxygen matrix. These results and recent experiments of Kulikov et al. on the temperature dependence of the ñₙ ozone band show that the interpretation of the experiments given in refs S2 and S3 should be reconsidered. For the ozone dimer (O₃)₂, the second stable conformation found in the present work can potentially be registered in the gas phase and in the matrix.

ASSOCIATED CONTENT

Supporting Information

The total and relative energies, vibrational frequencies, Cartesian coordinates for the reported structures. This material is available free of charge via the Internet at http://pubs.acs.org