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Theoretical characterization of the photochemical reaction $\text{CO}_2 + \text{O}(^3\text{P}) \rightarrow \text{CO} + \text{O}_2$ related to experiments in solid krypton

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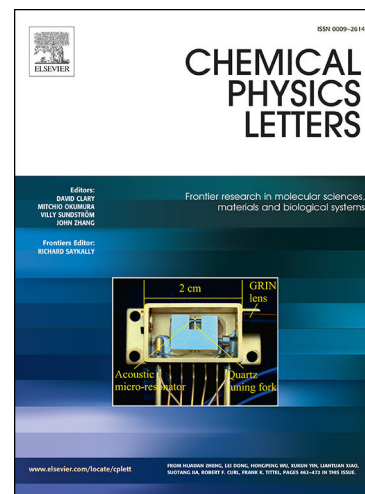
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Theoretical characterization of the photochemical reaction $\text{CO}_2 + \text{O}(^1\text{P}) \rightarrow \text{CO} + \text{O}_2$ related to experiments in solid krypton

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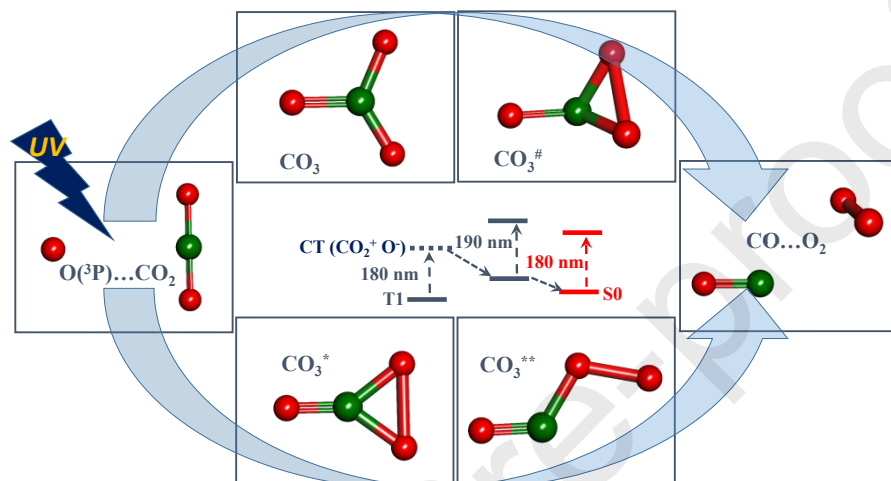
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Keywords: carbon dioxide, atomic oxygen, intermolecular complexes, matrix isolation, photochemistry, excited states, quantum chemistry

Highlights

- T-shape van der Waals complex $\text{CO}_2 \dots \text{O}(^3\text{P})$ presumably formed in solid Kr is characterized
- Excitation of $\text{CO}_2 \dots \text{O}(^3\text{P})$ leads to the intermediate CO_3 via the charge-transfer state
- Various scenarios describe decomposition of CO_3 to $\text{CO} + \text{O}_2(^3\Sigma_g^-)$ in Kr matrices
- High-level quantum chemistry methods are used in simulations

Graphical abstract**Abstract**

Formation and decomposition of the complex of carbon dioxide and atomic oxygen are characterized by quantum chemistry methods aiming to rationalize experimental studies in solid krypton. The observed FTIR spectra reflected the temporal evolution of the system after irradiation showing the bands of reactants, intermediates and products. Advanced quantum chemistry calculations show that the T-shape complex $\text{CO}_2 \dots \text{O}(^3\text{P})$ can be formed in the matrix. Its excitation by the 193 nm light results in the charge-transfer state $\text{CO}_2^+ \dots \text{O}^-$, which evolves to the reaction intermediate CO_3 . The latter species decomposes to $\text{CO} + \text{O}_2$ following pathways on the excited state energy surfaces.

1. Introduction

The interest in reactions of carbon dioxide with oxygen is explained by an importance of transformations with CO₂ in planetary atmospheres [1] as well as of the recent efforts in carbon dioxide reduction using photocatalytic conversion of CO₂ to CO [2]. In 2017, Dr. Khriachtchev proposed to study a photochemical reaction $\text{CO}_2 + \text{O} (^3\text{P}) \rightarrow \text{CO} + \text{O}_2$ by performing experiments in solid krypton matrices and quantum-chemical simulations. He supposed that this reaction might follow a mechanism similar to the photochemical synthesis of hydrogen peroxide from the H₂O...O(³P) van der Waals complex via the charge-transfer step as revealed in his previous works [3-5]. Unfortunately, a full-scale concerted experimental-theoretical study of this reaction has not been completed; therefore, we report here primarily the results of quantum-chemical simulations related to the subject.

Experimentally, the formation and decomposition of the CO₂...O(³P) complex was achieved by 193 nm photolysis of the N₂O/CO₂ mixture in the low-temperature krypton matrices, followed by annealing. The observed FTIR spectra reflected the temporal evolution of the system showing the bands of the CO₂ and CO₂...O(³P) species. Subsequent 193 nm irradiation resulted in decomposition of the latter complex giving the products CO + O₂ (³Σ_g⁻). A tentative proposal on the mechanism is that the carbon trioxide intermediate is formed via a high-energy charge-transfer state CO₂⁺...O⁻, and the CO₃ species decomposes to the reaction products.

From the theoretical side, reactions of carbon dioxide with oxygen atoms and properties of the carbon trioxide species were characterized by quantum chemistry methods in two papers. In 1993, Froese and Goddard [6] computed portions of the lowest singlet and triplet potential energy surfaces in the CO₃ system and located several stationary points corresponding to the stable species and transition states. Geometry structures were optimized using the SCF/6-31G* and MP2 methods, and the energies at the located points were also evaluated using MP4 and quadratic configuration interaction method QCISD(T). In 2004, Bennett et al. [7] reported the results of experimental and computational studies of CO₃ species. Local minima and transition states on the lowest singlet and triplet states of CO₃ were optimized using the CASSCF(16/13)/6-311G* method, and the energies at the stationary points were recomputed using the multireference configuration interaction method MRCI with the extended basis set. Photo-induced chemical reactions of carbon dioxide with oxygen were not considered previously.

2. Experimental and Computational Protocols

The N₂O/CO₂/Kr mixtures were prepared with concentration ratios of ~1/1/1000 and 1/0.2/1000. Carbon dioxide (AGA, 99.995%), nitrous oxide (99.9999%, AGA), and krypton (≥99.9999%, AGA) were used as supplied. The gas mixtures were deposited onto a CsI window

held at 20 K in a closed-cycle helium cryostat (KDK-408DZ, Sumitomo Heavy Industries, Ltd.). The matrix thickness was ~ 50 -100 μm . The Fourier transform infrared (FTIR) spectra in the 4000–500 cm^{-1} range were measured at 4.3 K with a Bruker Vertex 80 spectrometer by coadding 500 scans at a spectral resolution of 1 cm^{-1} . The matrix isolated species were photolyzed at 4.3 K by ArF excimer laser (MSX-250, MPB) operating at 193 nm ($\sim 10 \text{ mJ cm}^{-2}$, 1 Hz). After photolysis, the matrices were annealed at 25 K (typically, for 5 min) and then cooled down to 4.3 K for spectral measurements. The annealing products were irradiated at 193 nm with the excimer laser.

Equilibrium geometry configurations of the gas-phase species considered in this work (CO_2 , $\text{CO}_2\cdots\text{O}$, CO_3 , $\text{CO}\cdots\text{O}_2$) in either triplet or singlet electronic states were optimized at the MP2 and CCSD levels using the quantum chemistry packages Firefly [8] and QChem [9]. The cc-pVTZ basis set was utilized in all calculations; however, we checked for CO_2 and $\text{CO}_2\cdots\text{O}(^3\text{P})$ systems that the results obtained with the cc-pVQZ basis set were almost indistinguishable from those with cc-pVTZ (e.g., differences in vibrational frequencies were within 3 cm^{-1}). In the case of triplet states, the UMP2 method was applied using numerical algorithms implemented in Firefly [8].

Vibrational frequencies and the corresponding IR intensities were estimated in the harmonic approximation. To correct the computed frequencies to be compared with the observed band maxima in the krypton matrices we applied the scaling factor 0.97. The latter value was recommended in the previous combined experimental and theoretical study of transformations in the matrix isolated $\text{H}_2\text{O}\cdots\text{O}$ species [5].

Vertical excitation energies and dipole transition energies in the $\text{CO}_2\cdots\text{O}$ complex were computed, first, using the complete active space self-consistent field (CASSCF) method by distributing 16 electrons over 11 active orbitals, second, computing corrections within the extended multiconfigurational quasidegenerate perturbation theory in the second order (XMCQDPT2) [10]. The cc-pVTZ basis sets were applied. Scans over the excited state potential energy surfaces were performed using the numerical algorithms in XMCQDPT2. Excited state calculations were carried out using Firefly [8].

3. Results and Discussion

The deposited samples show characteristic absorptions of matrix-isolated carbon dioxide and nitrous oxide molecules as reported previously [11-13]. A small amount of their aggregates is also present [14, 15]. The carbon dioxide infrared-active fundamentals are collected in Table 1. The 193 nm irradiation mainly decomposes N_2O , producing O atoms and inert N_2 molecules whereas the CO_2 concentration remains practically unchanged. The typical percentage of the decomposition of N_2O was approximately 85–95%. Thermal annealing at 25 K activates the

mobility of O atoms in solid krypton [5] and leads to the appearance of two new bands at 2343.4 and 654.8 cm^{-1} . These bands are assigned to the T-shaped structure of the $\text{CO}_2\cdots\text{O}(^3\text{P})$ complex (Figure 1 and Table 1). Upon new 193 nm irradiation, the $\text{CO}_2\cdots\text{O}(^3\text{P})$ complex decomposes and the appearance of CO (2135.8 cm^{-1}) and a small amount of CO_3 (2039.4 cm^{-1}) is observed.

Table 1. Vibrational frequencies of the minimum energy species and experimental band positions in krypton matrices (cm^{-1}). IR intensities (km/mol) are in parentheses. Two right columns show the computed frequencies of the CO_3 species reported in Refs [6, 7].

	CCSD	MP2	Scaled MP2	Experiments in krypton	Ref [7] ^b	Ref [6] ^c
CO_2 singlet	685 (0.8) 2434 (17)	629 (0.6) 2423 (13)	2350	660.5 2336.7/ 2340.6		
$\text{CO}_2\cdots\text{O}$ triplet	682 (1.8) 684 (1.0) 2430 (17)	656 (1.6) 660 (0.8) 2418 (23)	2345	2343.6		
CO_3 singlet	589 (0.2) 688 (0.8) 692 (0.3) 1022 (1.6) 1142 (0.3) 2121 (14)	563 (0.2) 676 (0.6) 682 (0.4) 1078 (3.5) 1095 (0.3) 2057 (12)	1995	2039.4	506 575 671 1009 1050 2041	532 624 637 1036 1051 1967
CO_3 triplet		571 (2.2) 588 (0.1) 787 (2.8) 1095 (0.0) 1558 (3.9) 2000 (16)	1940			

^a This work, the strongest component of split bands is given in bold

^b Ref [7]: CASSCF values with a scaling factor 0.98

^c Ref [6]: MP2 values with a scaling factor 0.95

The computed minimum energy structures of the $\text{CO}_2\cdots\text{O}(^3\text{P})$ van der Waals complex and of the CO_3 species in the lowest energy triplet and singlet states are shown in Fig. 1. Table 1 lists the computed frequencies of the minimum energy structures.

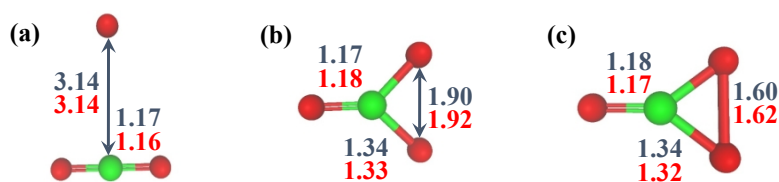


Figure 1. Equilibrium geometry configurations of the triplet state complex $\text{CO}_2\cdots\text{O}$ (panel (a)) and of the CO_3 molecule in the triplet (panel (b)) and singlet (panel (c)) states. Here and in all figures, carbon and oxygen atoms are colored green and red, respectively. The distances (in Å) are

obtained in the MP2/cc-pVTZ (top levels, dark blue) or in the RI-CCSD/cc-pVTZ (bottom levels, red) approaches.

In our calculations, the energy of the triplet state species CO_3 is above the level of $\text{CO}_2\cdots\text{O}(^3\text{P})$ at 33.8 kcal/mol (35.8 kcal/mol with ZPE) in the UMP2 approach, and 31.4 kcal/mol (31.3 kcal/mol with ZPE) in the CCSD approximation. Previous works reported the energy of the corresponding triplet state CO_3 isomer with respect to the $\text{CO}_2+\text{O}(^3\text{P})$ level at 23-24 kcal/mol (the T8 structure in Ref [6] obtained in QCISD(T)//MP2 calculations, and the t1 structure in Ref [7] obtained in MRCI//CASSCF calculations). The energy of the singlet state CO_3 computed at the CCSD level is 7.8 kcal/mol higher than that of the lowest energy triplet state. Calculations in Ref [6] for the structure S2 led to this energy gap about 4.0 kcal/mol, whereas calculations in Ref [7] reported that their s1 singlet state structure of CO_3 was almost degenerate with the $\text{CO}_2+\text{O}(^3\text{P})$ triplet state species. We conclude that the results of our calculations for the carbon trioxide species basically agree with the previous theoretical data [6, 7]. The largest deviations from the values reported in [6, 7] refer to the energies of CO_3 in the triplet state. We expect that the results of the CCSD approach used in this work are superior to those obtained with the CI-based estimates performed in [6, 7].

Comparison of the columns “Scaled MP2” and “Experiments in krypton” in Table 1 shows a good agreement of the computed and observed vibrational frequencies. According to these data, most likely, the singlet state CO_3 species was observed in experiments.

The optimized gas-phase structure of the ground state complex $\text{CO} + \text{O}_2(^3\Sigma_g^-)$ corresponds to a system of two separated diatomic molecules, in which the shortest intermolecular distance $\text{O}(\text{CO})-\text{O}(\text{O}_2)$ is about 3.3 Å. This complex is of a limited interest for the purposes of this work.

In the $\text{CO}_2\cdots\text{O}(^3\text{P})$ equilibrium geometry we computed the vertical excitation energies from the ground triplet state (denoted T1 in this work) to a variety of triplet states using the CASSCF and XMCQDPT2/CASSCF methods. The CASSCF wavefunctions corresponded to the distribution of 16 electrons over 11 active orbitals, that was sufficient to recognize the levels of the charge-transfer (CT) states $\text{CO}_2^+\cdots\text{O}(^2\text{P})$. Accordingly, we carefully analyzed the multiconfigurational compositions and the optimized molecular orbitals for a manifold of triplet states. At the CASSCF level, the requested CT states could be identified only as highly lying roots in the multiconfigurational expansion. The picture changed dramatically when the XMCQDPT2 approach was applied on the top of the CASSCF representation. In this scheme the CT states lowered down considerably; they were recognized as the states lying between the 5th and 10th roots. Fig. 2 illustrates the optimized molecular orbitals and their occupation numbers in the T5 state clearly showing the charge-transfer assignment of this state.

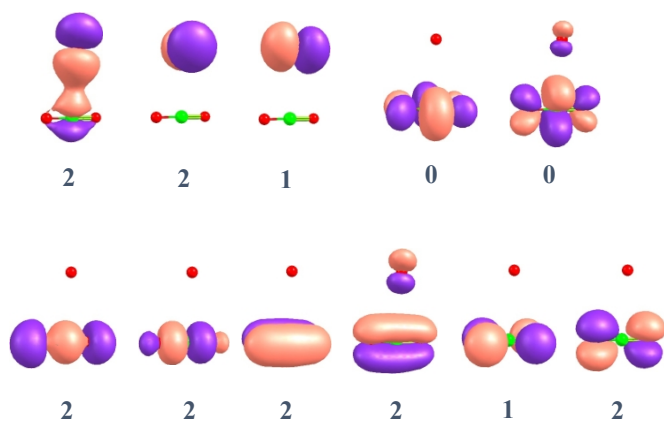


Figure 2. Molecular orbitals and their occupation numbers (below each picture) in the charge-transfer T5 state of the van der Waals complex $\text{CO}_2 \dots \text{O}(^3\text{P})$ in the XMCQDPT2/CASSCF(16/11) approach.

What is more important, the energy difference between the T1 ground state and the T5 state is 7.15 eV (corresponding to the 173 nm wavelength) as computed with the cc-pVTZ basis set, and 6.87 eV (180 nm) as computed with the cc-pVQZ basis set. The corresponding transition dipole moment T1→T5 is 0.14 a.u. In experiments, the 193 nm irradiation (corresponding to the 6.42 eV energy gap) was used to stimulate the photo-induced transformations of the $\text{CO}_2 \dots \text{O}(^3\text{P})$ complex. Taking into consideration that computational models refer to the gas-phase conditions, while experiments refer to the polarizable continuum of low-temperature solid krypton, we believe that the XMCQDPT2/CASSCF(16/11) level provides an adequate description of the system.

Therefore, we examined the excited-state energy relief in the triplet state after the vertical T1($\text{CO}_2 \dots \text{O}(^3\text{P})$)→T5($\text{CO}_2^+ \dots \text{O}(^2\text{P})$) excitation. Upon approaching the oxygen atom to the CO_2 partner (see Fig. 1a) we computed the gradually lowering energies in the XMCQDPT2/CASSCF(16/11)/cc-pVTZ approximation and analyzed the multiconfigurational expansions and orbitals at every step. The system consistently passed several crossings of the triplet state potential energy surfaces and finally evolved to the vicinity of the local minima on the ground state triplet surface corresponding to the structure of the CO_3 species, T1(CO_3). Optimization of its geometry parameters at the UMP2/cc-pVTZ level and calculation of the harmonic frequencies (shown in Table 1) enables the characterization of this stationary point. This is the triplet state CO_3 system briefly mentioned in the previous simulations (denoted as T8 in Ref [6] or t1 in Ref [7]). The left side of Fig. 3 illustrates the pathway from the $\text{CO}_2 \dots \text{O}(^3\text{P})$ complex to the triplet state carbon trioxide via excitation to the charge-transfer state.

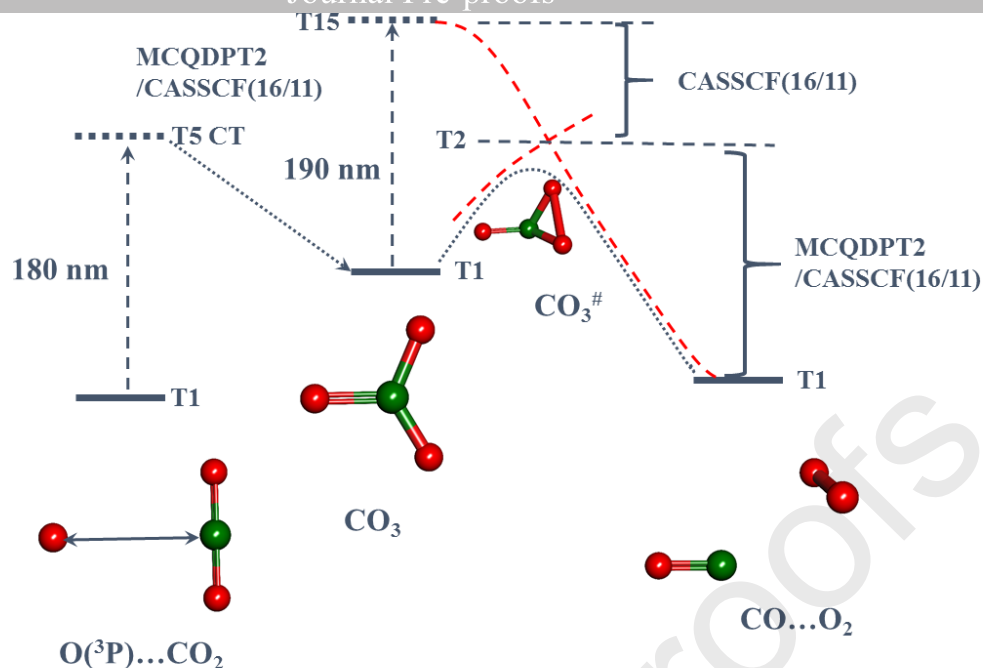


Figure 3. The scheme of the photoinduced reaction $\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$ in the triplet state.

The fate of the thus formed CO_3 species was traced along several directions. First of all, it can easily decompose back to carbon dioxide and atomic oxygen. We remind that its energy is more than 30 kcal/mol higher in our calculations (or about 23 kcal/mol in the literature [6, 7]) than that of the $\text{CO}_2\dots\text{O}(^3\text{P})$ system. Our estimates of the barrier of such decomposition on the triplet state surface at the CASSCF(16/11)/cc-pVTZ level give 6 kcal/mol. According to the calculations of Ref [6], this barrier is about 10 kcal/mol, while Ref [7] reports 12 kcal/mol. Therefore, it is hard to expect a long-lived triplet state carbon trioxide molecule in solid matrices.

A more intriguing scenario is prompted by the experimental protocol, namely, the observation of the photo-reaction products, $\text{CO} + \text{O}_2$, after second 193 nm irradiation of the samples. The central part in Fig. 3 illustrates the energy diagram showing that the triplet state CO_3 species can be excited by this energy into the high energy triplet state T15 (the XMCQDPT2 results). It is unfeasible to examine evolution of the system in this state rigorously; however, it is possible to examine multiconfigurational wavefunctions and orbitals in various electronic states along the assumed reaction coordinate at the CASSCF level. We performed a series of CASSCF calculations each time switching between states until the second triplet state T2 potential energy surface was encountered. The Firefly software [8] allows one to locate the conical intersection point using the XMCQDPT2 numerical algorithms. This point is denoted $\text{CO}_3^\#$ in Fig. 3. The energy gap between the points CO_3 and $\text{CO}_3^\#$ on the ground state triplet potential energy surface is approximately 90 kcal/mol. Geometry optimization of the system starting from the $\text{CO}_3^\#$ species

in the T1 state carried out at the XMCQDPT2 level allowed us to arrive to the reaction products $\text{CO}\dots\text{O}_2$ (${}^3\Sigma_g^-$) shown in the right bottom panel in Fig. 3.

One more possibility to connect the reaction intermediate CO_3 and products $\text{CO}\dots\text{O}_2$ is to explore coupling of the triplet and singlet states in the system. As shown in Fig. 4, the lowest energy triplet state structure CO_3 is characterized by fairly close energies of the triplet T1 and singlet S0 states. Optimization of geometry parameters of CO_3 in the lowest singlet state led to another C_{2v} type species denoted here as CO_3^* (also shown in Fig. 1c). This is a structure described in the previous works, namely, the s1 isomer of CO_3 in Ref [7] or the S2 isomer in Ref [6].

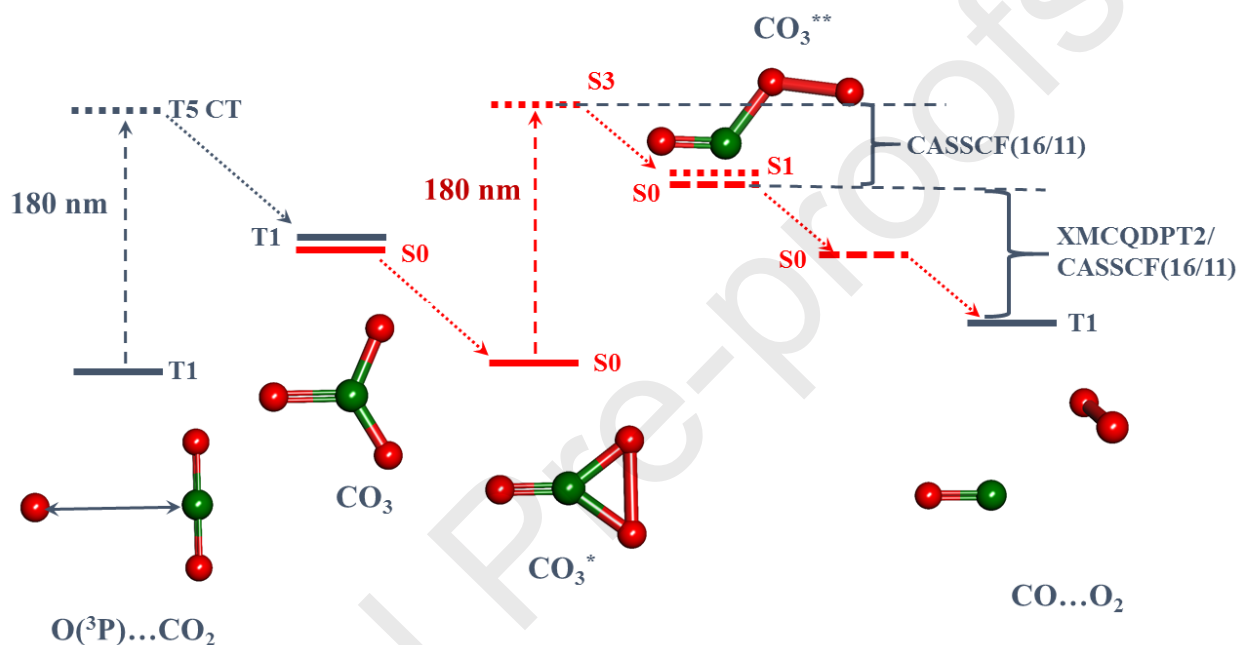


Figure 4. Tentative scheme of the photoinduced reaction $\text{CO}_2+\text{O}\rightarrow\text{CO}+\text{O}_2$ assuming the triplet-singlet transitions in the reaction intermediates.

Importantly, the CO_3^* species can be excited by the 6.9 eV light (~ 180 nm, close to the experimentally explored 193 nm) to reach the S3 state (the 4th singlet state), evolution from which finally leads to the products (Fig. 4). We again applied the strategy to analyze the route from S3 to the second singlet state S1 using the CASSCF method followed by XMCQDPT2 geometry optimization. This is a less probable channel due to the low transition dipole moment of electronic excitation $\text{S0} \rightarrow \text{S3}$ and expected low probabilities of the singlet-triplet transitions, but may be also operative.

To summarize, theoretical calculations provide support to the mechanism of the observed photo-induced matrix reaction $\text{CO}_2+\text{O}({}^3\text{P})\rightarrow\text{CO}+\text{O}_2$ that assumes involvement of the highly excited charge-transfer states. An original idea of Dr. Khriachtchev that the quasilinear (or the chain-like) structure of carbon trioxide might be formed among reaction intermediates followed

by easy decomposition to CO and O₂ was carefully examined in simulations. However, we failed to find a suitable reaction channel. Fig. 4 shows a structure of such shape which is denoted CO₃**⁺; however, it corresponds to the conical intersection point S1/S0, but not to the reaction intermediate.

4. Conclusion

We report here the following new aspects of the reactions of carbon dioxide with atomic oxygen initiated by irradiation of the CO₂/N₂O mixture in solid krypton. High-level quantum chemistry calculations show that the T-shape van der Waals complex CO₂...O(³P) can be formed in the matrix. Its excitation by the 193 nm light results in the charge-transfer state of the complex CO₂⁺...O⁻, which evolves to the reaction intermediate CO₃. The latter species can decompose to the CO + O₂ products following pathways on the excited state energy surfaces.

5. Acknowledgment

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Веня Л. Григоренко: Conceptualization, Investigation

Luís Duarte: Investigation

Igor V. Polyakov: Investigation

Alexander V. Nemukhin: Writing – Reviewing and Editing

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