The lowest doublet and quartet potential energy surfaces involved in the N(4\(S\))+O\(_2\) reaction. I. Ab initio study of the \(C_s\)-symmetry (\(^2\!A',\ 4\!A'\)) abstraction and insertion mechanisms

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In this work we have carried out \textit{ab initio} complete active space self-consistent-field (CASSCF) calculations, second-order perturbation calculations based on CASSCF wave functions (CASPT2), uncontracted multireference configuration interaction calculations, and some density functional calculations with standard correlation-consistent Dunning basis sets and atomic natural orbital basis sets on the lowest \(^2\!A'\) and \(^4\!A'\) potential energy surfaces involved in the title reaction. The ground \(^2\!A'\) surface has an average energy barrier of 5.3 kcal/mol in the CASPT2 complete basis set limit. A peroxy NOO minimum is found in agreement with preceding \textit{ab initio} works, which seems to play an important role in the opening of a double microscopic mechanism: direct \(C_s\) abstraction and indirect \(C_s\) insertion through the NO\(_2\)(X \(^2\!A_1\)) molecule. The ground \(^4\!A'\) surface shows an average energy barrier of 13.5 kcal/mol in the CASPT2 complete basis set limit. Despite this excited surface displays another peroxy minimum, in this case only a direct \(C_s\)-abstraction mechanism can be expected. The present results improve previous high quality \textit{ab initio} studies and provide lower energy barriers in both potential energy surfaces, which would produce larger total thermal rate constants in better agreement with experimental data. Finally, it is demonstrated that the N and O 2s electron correlation cannot be neglected as it produces a significant decrease in both energy barriers.

I. INTRODUCTION

The elementary gas-phase reaction of N(4\(S\)) with molecular oxygen,

\[
\text{N}(4\!S) + \text{O}_2(X^{3\!S_g^-}) \rightarrow \text{O}(3\!P) + \text{NO}(X^{2\!II}),
\]

\[\Delta H_0^{\text{298}} = -32.09 \text{ kcal/mol} \tag{1}\]

(Ref. 1) and its reverse reaction play an important role in atmospheric chemistry. This reaction is a source of infrared chemiluminescence in the upper atmosphere.\(^2\) High temperature studies of the kinetics and dynamics of the N(4\(S\))+O\(_2\) and N(4\(S\))+NO reactions and their reverse ones are very important for the understanding of the chemical and physical phenomena taking place during the re-entry of spacecrafts into the Earth’s atmosphere,\(^3\) where nonthermal equilibrium conditions between the different degrees of freedom may play an essential role. Reaction (1) with hot N atoms provides an additional mechanism for the production of nitric oxide in the earth thermosphere.\(^4\) This reaction is also of interest in the context of combustion of hydrocarbon–air mixtures.\(^5\)

In several preceding papers\(^6\)–\(^10\), we have presented different theoretical approaches to this reaction and we have also given a detailed review of the main experimental and theoretical data that have been published for this reaction. Thus, in the current introduction we will summarize only the principal information and we will update that with the latest and the most significant contributions to this reaction.

Experimental kinetics studies are available dealing with resembling thermal rate constants in a wide interval of temperatures: \(k = 1.5 \times 10^{-11} e^{-3600T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 280–910 K (Ref. 11) or \(1.5 \times 10^{-14} e^{-3270T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 298–5000 K.\(^12\) Measurements of NO vibrational distributions, populated between \(v = 0–7\), show some important differences on their shapes for reactants at room temperature.\(^13\)–\(^17\)

Several \textit{ab initio} studies have been reported on the ground \(^2\!A'\) and the first excited \(^4\!A'\) potential energy surfaces (PES) involved in this reaction. Thus, CASSCF and multireference contracted CI calculations with large Gaussian basis sets\(^18\) have been carried out for both PESs aimed at characterizing the transition states and minimum energy reaction paths. The same \textit{ab initio} method but with large ANO basis sets were also used in a more recent theoretical study of the ground \(^2\!A'\) PES.\(^19\) Several studies have dealt with the controversy about the existence of a NOO peroxy isomer on the ground doublet PES\(^20\)–\(^22\) that could have some influence in the studied reaction.

In order to study the kinetics and the dynamics of this reaction, several analytical fits of the lowest doublet PES have been reported in previous works based mainly in the before mentioned \textit{ab initio} data.\(^18\) Most of them\(^23\)–\(^25\) are based on the analytical form (many-body expansion) and parameters (diatomic terms and reference structure of the three-body term) employed in our first study,\(^6\) and made use of the
**II. THEORETICAL METHODS**

The *ab initio* calculations presented in this work have been performed with the MOLCAS 4.1 (Ref. 28) package of programs. The complete active space self-consistent-field method (CASSCF)\(^29,30\) was employed throughout this study, always choosing the lowest root in \(C_s\) symmetry for both the doublet and the quartet PESs (i.e., \(2\text{A}^\prime\) and \(4\text{A}^\prime\), which correlate reactants and products of reaction (1)). The location of each stationary point geometry on the PESs was achieved by optimization searches of both minima and transition states employing analytic CASSCF gradients. Full characterization of them was effected by calculating the numerical Hessian matrix at the optimized geometries. Calculations at second-order perturbation theory based on a zeroth-order CASSCF wave function (CASPT2 method) using the standard correction (i.e., std) or some \(G_s(i=1,2,3)\) variants\(^31\) as implemented in MOLCAS 4.1 were applied to refine the stationary points obtained at the CASSCF level. In some cases a grid of CASPT2 points was generated to search directly the stationary point. Thus, local fits were performed by means of bicubic splines\(^32\) or Taylor expansions in the bond angle together with symmetry adapted internal coordinates expansion in the bond lengths to obtain the optimal geometry and the harmonic frequencies at CASPT2 level by using the SURVFIT code of molecular rovibrational analysis.\(^33\) More details of the procedure used can be found in a recent paper of our group.\(^34\)

Two different active spaces of the NO\(_2\) system were used in the present study: (a) the full-valence active space, i.e., all the atomic 2\(s\) and 2\(p\) electrons are distributed among the corresponding derived bonding and antibonding molecular orbitals (MO) [i.e., CAS (17,12)] and (b) a smaller active space with only the 2\(p\) electrons [i.e., CAS (11,9)]. This latter active space has been assumed to be accurate enough for this system in some preceding papers;\(^18,19,22\) in both cases the natural MO occupation has been checked for all stationary points. The CAS (17,12) comprising 17 electrons in 12 orbitals generates 28503 and 20376 configuration state functions (CSF) for the \(2\text{A}^\prime\) and \(4\text{A}^\prime\) PESs, respectively, while the CAS (11,9) produces only 3048 and 1878, respectively.

CASPT2 and CASSCF calculations have been performed checking the effect of the correlation energy of the three atomic 1\(s\) or 2\(s\) electrons; previously, the 1\(s\) and 2\(s\) orbitals were optimized at the CASSCF level. The results were very similar to those obtained previously without the 1\(s\) frozen core option. In all cases the barrier energies were around 10% higher if the 1\(s\) orbitals were kept frozen. 2\(s\) valence orbitals were only kept frozen in some CASPT2 calculations to compare with earlier CASSCF followed by multireference contracted CI (CCI) calculations.\(^18\)

The standard correlation-consistent (cc-pVnZ and aug-cc-pVnZ, \(n=D,T,Q,5\)) Dunning's basis sets\(^35\) and small and large atomic natural orbital (AN0) basis sets\(^36\) were used in the present study. The basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 1.0, as developed and distributed by the Molecular Science Computing Facility.\(^37\)

Some density functional theory (DFT) studies by using the unrestricted B3LYP method as implemented in the GAUSSIAN 98 (Ref. 38) code were adopted to facilitate the search of the stationary points.

Supermolecule calculations were considered in the determination of all energies in both the *ab initio* and the DFT methods.

Recent studies on similar reactions [e.g., N(\(^2\)D) + NO (Ref. 34) and N(\(^2\)D) + O\(_2\)\(^39\) systems] using the present methods have shown that they are accurate enough to provide a good description of them in comparison with experimental data or larger calculations.

**III. RESULTS AND DISCUSSION**

**A. Stable molecules and reaction exoergicity**

A first verification of the degree of accuracy of the theoretical approach has been carried out by calculating the properties of the diatomic and NO\(_2\)(\(X^2\text{A}^1\)) molecules, and the exoergicity of reaction (1). Thus, Table I summarizes the
bond length, the harmonic vibrational frequency and the dissociation energy of both diatomic molecules at different ab initio levels. The comparison of the calculated geometries with the experimental data shows a small effect of the size and quality of the basis set on the optimized bond length, although the most remarkable enhancement is produced when the geometry is optimized directly at the CASPT2 G2 level. The results are comparable for both types of basis sets (i.e., ANO and cc-pVnZ/aug-cc-pVnZ) for a similar number of basis functions (e.g., compare the ANO-A basis set with the cc-pVTZ one both with a total number of 90 basis functions). An excellent agreement was also obtained for the harmonic frequencies. However, the description of both O₂ and NO dissociation energies was somewhat worse. First, the introduction of the dynamical correlation energy by means of the CASPT2 method was essential for a reasonable description. Second, the G₁ variants gave similar results although much better than the standard Fock matrix one, as it should be expected. The O₂ dissociation energy presented a significant error (4.5% with respect to the experimental value) even at the highest ab initio calculation level (i.e., CASPT2 G2(17,12)/aug-cc-pVTZ method), that originated mainly the
discrepancy in the exoergicity with respect to the experimental value. The differences arose from the use of two different active spaces were very small as should be expected owing to the high occupation number [over 1.99 in CAS(17,12)] of two of the natural MOs in this asymptotic region of the PES.

The difficulty in the O₂ theoretical treatment is well known and can only be amended with very refined and computationally expensive \textit{ab initio} calculations with inclusion of complete basis set (CBS) limits.⁴¹,⁴² However, we believe that is not crucial in the context of the present study, which tries to account for all the stationary points of the lowest doublet and quartet PESs at the same level, with a foremost importance concerning the energy barriers.

On the other hand, DFT calculations at the UB3LYP/aug-cc-pVTZ level offered good results and improved substantially the reaction exoergicity.

Table II presents the results for the NO₂(\(X^2\)A₁) molecule. In spite of the calculated geometry and harmonic frequencies were very similar for both actives spaces [i.e., (11,9) and (17,12)] and match very well the experimental values, important differences were observed in the dissociation energies. The increase of the active space size improved significantly the calculated dissociation energies, although was necessary the introduction of the dynamical correlation energy by means of the CASPT2 method to accurately reproduce the experimental values. The reference weight into the CASPT2 wave function was high enough to describe properly the molecule [i.e., approximately 90% at CAS(17,12)]. The importance of the higher active space was confirmed by the occupation of the 12 natural MOs: \(a₁:1.998, 1.984, 1.980, 1.039, 0.0424, b₁:1.965, 0.115, a₂:1.923,\) and \(b₂:1.998, 1.966, 1.960, 0.0284\). The nitrogen 2s contribution in several active MOs was important in the description of the NO₂ molecule, especially for bent geometries as it has been also observed in previous works.⁴⁹ On the other hand, the multireference character of the wave function of the NO₂ molecule can be clearly illustrated taking into account the three most important CSFs and their coefficients:

\[
\begin{align*}
-0.943 & \cdots (3a₁)^2(4a₁)^2(5a₁)^2(6a₁)^1(7a₁)^0(1b₁)^2(2b₁)^0(1a₂)^2(2b₂)^2(3b₂)^2(4b₂)^2(5b₂)^0, \\
-0.144 & \cdots (3a₁)^2(4a₁)^2(5a₁)^2(6a₁)^1(7a₁)^0(1b₁)^2(2b₁)^0(1a₂)^2(2b₂)^2(3b₂)^2(4b₂)^2(5b₂)^0, \\
0.125 & \cdots (3a₁)^2(4a₁)^2(5a₁)^2(6a₁)^1(7a₁)^0(1b₁)^2(2b₁)^0(1a₂)^2(2b₂)^2(3b₂)^2(4b₂)^2(5b₂)^0.
\end{align*}
\]

The present study improves the previous \textit{ab initio} results for NO₂ molecule as it can be observed in Table II.

B. Characterization of the lowest \(2^1\)A\(^{+}\) potential energy surface

The geometries, frequencies, and energies relative to reactants, N(\(^4\)S) + O₂, for all the stationary points characterized in the \textit{ab initio} (i.e., CASSCF and CASPT2) and DFT (i.e., UB3LYP) levels for the ground doublet PES are given in Tables III, IV, and V. Figure 1 shows the MERPs connecting reactants and products. The attack of the N(\(^4\)S) atom to the O₂ molecule produces a bent transition state (TS1) with the highest energy barrier among the MERPs, which leads to a shallow NOO peroxy minimum (MIN1) previously reported in the literature. ²¹,²²

The system can directly produce O(\(^3\)P) + NO after surmounting another transition state (TS2) or can evolve through another shallow NOO minimum (MIN2) and through the much deeper ground state NO₂(X^2A₁) molecule after surmounting two transition states (TS3 and TS4). No barrier seems to exist between NO₂ molecule and products. Table III presents a comparative study about the properties of TS1. First of all, CASSCF calculations with different basis sets and the lower active space (11,9) yield similar geometries, frequencies and a very small decrease in the energy barrier. Nevertheless, the increase in the active space to (17,12) produces a significant enlargement of the NO distance (ca., 0.025 Å) and also an additional energy barrier reduction. The introduction of the dynamical correlation energy through the CASPT2 method (std or G2) originates a dramatic decrease in the energy barrier. In some cases the obtained value [e.g., 4.14 kcal/mol at CASPT2(17,12) G2/aug-cc-pVTZ] is too small in comparison with a value compatible with the experimental activation energy [i.e., 7.2 kcal/mol within 280–910 K (Ref. 11)]. Due to this fact, and also taking into account previous published results (see Table III) that evidence the important effect of the dynamical correlation energy into the NO distance optimization of this TS [e.g., 1.821 Å at MR-CCI+Q/CASSCF(11,9)/[11s6p/5s3p2d1f] or 1.825 Å at MR-ICCI+Q/CASSCF(9,8)/cc-pVTZ²²], we carried out a numerical optimization at the CASPT2(17,12) G2 level. An optimum NO distance of 1.825 Å was obtained for TS1, which produced an energy barrier of 4.70 kcal/mol [5.00 kcal/mol including zero point energy (ZPE) differences].

A detailed study of the energy barrier of TS1 has been made by increasing the quality of the basis set at the optimum CASPT2(17,12) G2 geometry. The basis set dependence is usually well described by a simple exponential-like function ³⁰ of the form

\[
\Delta E_n^\dagger = \Delta E_\infty^\dagger + B e^{-C n},
\]

where \(n\) is the cardinal number of the basis set (2, 3, 4, and 5 for DZ, TZ, QZ, and 5Z, respectively) and \(\Delta E_n^\dagger\) corresponds to the estimated complete basis set (CBS) limit as \(n \rightarrow \infty\). The estimated CASPT2(17,12) CBS limits for this
TABLE II. *Ab initio* and DFT properties of the NO$_2(X\:^2A_1)$ molecule.*

| Method          | Basis set$^a$ | $E$/a.u. | $R_{(NO)}$/Å | <ONO$/^b$ | $\omega_1$/cm$^{-1}$/ | $D_v$/kcal mol$^{-1}$/d |
|-----------------|---------------|-----------|--------------|----------|-----------------------|------------------------|
| CASSCF(11,9)    | ANO-A         | $-204.279$ 148 | 1.969 | 134.28 | 1336.73 | 758.36 | 1643.68 | 36.78 | 72.78 |
|                 | ANO-D         | $-204.283$ 923 | 1.959 | 134.23 | 1338.00 | 761.73 | 1642.64 | 37.50 | 73.63 |
|                 | cc-pVDZ       | $-204.270$ 210 | 1.2026 | 133.95 | 1342.90 | 752.37 | 1654.58 | 33.46 | 69.00 |
|                 | cc-pVTZ       | $-204.265$ 605 | 1.977 | 134.21 | 1335.73 | 758.95 | 1645.62 | 37.10 | 72.92 |
|                 | cc-pVQZ       | $-204.281$ 099 | 1.959 | 134.22 | 1340.21 | 762.90 | 1654.30 | 37.61 | 73.77 |
|                 | aug-cc-pVDZ   | $-204.221$ 811 | 1.237 | 133.93 | 1335.32 | 747.23 | 1641.91 | 55.37 | 70.75 |
|                 | aug-cc-pVTZ   | $-204.268$ 151 | 1.973 | 134.23 | 1331.92 | 759.00 | 1637.15 | 37.29 | 73.17 |
| CASPT2(11,9) std| cc-pVDZ       | $-204.595$ 240 | 67.17 | 88.73 |
|                 | cc-pVTZ       | $-204.819$ 314 | 76.54 | 99.07 |
|                 | cc-pVQZ       | $-204.932$ 603 | 78.29 | 101.42 |
|                 | aug-cc-pVDZ   | $-204.641$ 007 | 70.73 | 90.81 |
|                 | aug-cc-pVTZ   | $-204.841$ 480 | 79.23 | 101.79 |
| CASPT2(11,9) G2 | cc-pVDZ       | $-204.597$ 127 | 70.96 | 96.07 |
|                 | cc-pVTZ       | $-204.800$ 811 | 69.53 | 94.98 |
|                 | cc-pVQZ       | $-204.934$ 093 | 84.15 | 110.39 |
|                 | aug-cc-pVDZ   | $-204.642$ 824 | 76.24 | 99.00 |
|                 | aug-cc-pVTZ   | $-204.843$ 002 | 85.07 | 96.00 |
| CASPT2(17,12)   | ANO-A         | $-204.306$ 726 | 1.2035 | 134.01 | 1339.95 | 751.77 | 1614.86 | 48.56 | 86.71 |
|                 | ANO-B         | $-204.310$ 264 | 1.2028 | 133.95 | 1340.85 | 754.60 | 1614.98 | 49.05 | 87.21 |
|                 | cc-pVDZ       | $-204.235$ 397 | 1.2087 | 133.80 | 1348.46 | 746.83 | 1632.93 | 45.50 | 72.92 |
|                 | cc-pVTZ       | $-204.293$ 276 | 1.2043 | 133.95 | 1339.62 | 752.71 | 1618.38 | 48.93 | 86.91 |
|                 | cc-pVQZ       | $-204.308$ 694 | 1.2025 | 133.94 | 1343.13 | 755.82 | 1616.13 | 50.02 | 87.70 |
|                 | aug-cc-pVDZ   | $-204.249$ 666 | 1.2100 | 133.78 | 1341.69 | 742.21 | 1618.21 | 47.25 | 84.84 |
|                 | aug-cc-pVTZ   | $-204.295$ 723 | 1.2040 | 133.95 | 1335.76 | 753.15 | 1608.79 | 49.05 | 87.10 |
| CASPT2(17,12) std| cc-pVDZ       | $-204.594$ 659 | 65.14 | 87.97 |
|                 | cc-pVTZ       | $-204.817$ 849 | 75.84 | 98.03 |
|                 | cc-pVQZ       | $-204.930$ 986 | 75.89 | 108.36 |
|                 | aug-cc-pVDZ   | $-204.640$ 114 | 68.53 | 89.91 |
|                 | aug-cc-pVTZ   | $-204.839$ 859 | 76.81 | 100.59 |
| CASPT2(17,12) G2 | cc-pVDZ       | $-204.795$ 983 | 79.58 | 104.99 |
|                 | cc-pVTZ       | $-204.875$ 660 | 82.16 | 109.97 |
|                 | cc-pVQZ       | $-204.934$ 065 | 68.05 | 93.21 |
|                 | aug-cc-pVDZ   | $-204.816$ 027 | 77.85 | 104.35 |
|                 | aug-cc-pVTZ   | $-204.929$ 061 | 79.72 | 107.14 |
| CASPT2(17,12) G2 | aug-cc-pVTZ $^c$ | $-204.838$ 117 | 1.1965 | 134.30 | 1344.13 | 755.27 | 1677.17 | 80.69 | 107.52 |

Dunning [9s5p/4s3p1d] Dunning DZ+P $^c$UB3LYP

CISD$^g$
CASPT2(11,9)$^b$ $^d$
UB3LYP Experiment

| $^i$ | $^i$ | $^i$ | $^i$ | $^i$

$^a$CASPT2 energies at the CASSCF optimum geometries with the same basis set.
$^b$ANO basis set as in Table I.
$^c$Harmonic vibrational frequencies: $\omega_1$ (sym str, $a_1$), $\omega_2$ (bend, $a_1$), and $\omega_3$ (asymp str, $b_2$), respectively ($YZ$ taken as the molecular plane). Masses of the most abundant isotopes were used: $^{14}$N and $^{16}$O.
$^d$Dissociation energies to the O(3P) + NO and N(4S) + O$_2$ asymptotes, respectively.
$^e$CASPT2 G2 optimum geometries and harmonic vibrational frequencies obtained by using the SURVIBTM program (Ref. 33).
$^f$Reference 43.
$^g$Reference 44.
$^h$Reference 45. Properties derived from an analytical fit of 872 *ab initio* points.
$^i$Reference 46.
$^j$Reference 47.
$^k$Reference 1. Fundamental $v_1$ frequencies are reported.
$^l$Reference 48. Fundamental $v_1$ frequencies are reported.
$^m$Obtained by adding the experimental exoergicity (Ref. 40).

energy barrier were (a) 4.90 and 4.73 kcal/mol at the G2 level, and (b) 5.99 and 5.69 kcal/mol at the std level for the cc-pVnZ and aug-cc-pVnZ series, respectively, with a maximum error of $\pm 0.3$ kcal/mol, estimated by using other exponential functions. Therefore, similar CBS energy barriers were found for both series of basis sets. The main difference (ca., 1 kcal/mol) arises from the use of the G2 or the standard CASPT2 variants. However, these values are very close to
the energy barrier finally fitted in our previous analytical PES (i.e., 6.2 kcal/mol[10]), which was derived from ab initio data[18] and variational transition state rate constants which reproduced the experimental rate constants in a wide interval of temperatures (300–5000 K), with the inclusion of the k(4 A') contribution.

We have also calculated the TS1 energy barrier using the uncontracted multireference SD–CI (MR–CI) method with the inclusion of the Davidson correction (Q), based on the same CASSCF(11,9) MOs; 11 e have been correlated (1s and 2s electrons were frozen). We have done these calculations to verify the previous results of Walch and Jaffe[18] (Table III) and to show how those MR–CI+Q calculations overestimate energy barriers, specially when the 2s electrons are not correlated. We have obtained an energy barrier of 8.16 kcal/mol by using a MR–CI with 24 CSFs of reference (3,709.673 CSF in all for Cs symmetry). If the 2s electrons are neither correlated in the CASPT2(11,9) G2 calculations, the barrier increases to 8.07 kcal/mol, which is very similar to the mentioned MR–CI+Q value. Therefore, it is very important to correlate the 2s electrons in both the CASPT2 and MR–CI calculations, which produces lower energy barriers,
much closer to the value estimated from experimental data.

DFT calculations at the UB3LYP/aug-cc-pVTZ level give very good results [e.g., an energy barrier of 5.81 kcal/mol (6.03 kcal/mol including zero point energy differences)] and compare very well with the highest accurate ab initio calculations. Nevertheless, a large spin contamination was observed in TS1 ($S^2$) = 2.15 to be compared with the correct expectation value of 0.75.

Schaefer III et al., from an early ab initio study, proposed the existence of a NOO ($A^1$) peroxy isomer as a stable species that could play an important role in atmospheric chemistry. The same authors confirmed later this point by using much more accurate ab initio calculations. They found a very shallowly bound isomer, 85.3 kcal/mol over the NO$_2$ molecule at the CISD level (see Table I), although no TSs were reported for its dissociation. In a latter paper Walsh' checked the low stability of this minimum, separated from O($^3$P) + NO by an energy barrier of only 0.25 kcal/mol [at the MR–ICCI+Q/CASSCF(9,8) level without the inclusion of ZPE differences]. This energy barrier corresponds approximately to that of TS3 (Table V). Here we have found this peroxy minimum (MINI) at the CASSCF, CASPT2, and UB3LYP levels as is shown in Table IV. Geometry and frequencies are very similar to those previously obtained by the above-mentioned authors. We have obtained an energy with respect to the NO$_2$ molecule of 81.01, 86.14, and 84.99 kcal/mol at CASSCF(17,12)/aug-cc-pVTZ, CASPT2(17,12) G2/aug-cc-pVTZ, and UB3LYP/aug-cc-pVTZ levels, respectively.

The most important CSFs for this minimum are

Table V: Ab initio and DFT properties of several stationary points located on the $^3A^1$ PES.$^*$

| Method | Basis set | $R_{c(NO)}$/Å | $R_{c(OO)}$/Å | $<\text{NOO}/^\text{n}$ | $\omega_1$/cm$^{-1}$ | $\Delta E$/kcal mol$^{-1}$ |
|--------|-----------|---------------|---------------|-----------------|----------------|-----------------|
| TS2    | CASPT2(17,12) G2 | aug-cc-pVTZ  | 1.1428 | 1.5653 | 135.41 | 1660.03 | 574.86 | 619.69 | -21.94 |
|        | UB3LYP    | aug-cc-pVTZ  | 1.1324 | 1.5571 | 131.83 | 1748.03 | 540.27 | 455.75 | -21.53 |
| TS3    | CASPT2(17,12) G2 | aug-cc-pVTZ  | 1.1798 | 1.4739 | 114.72 | 1553.46 | 390.79 | 772.71 | -25.34 |
|        | UB3LYP    | aug-cc-pVTZ  | 1.1580 | 1.4942 | 111.76 | 1314.30 | 373.99 | 772.71 | -25.34 |
|        | MR–ICCI+Q/CASSCF(9,8)$^d$ | cc-pVTZ | 1.194 | 1.483 | 107.3 | 1714 | 602 | 484 | -14.33 |
| TS4    | CASPT2(17,12) G2 | aug-cc-pVTZ  | 1.1415 | 2.1468 | 90.15 | 1891.41 | 341.35 | 139.54 | -28.28 |
|        | UB3LYP    | aug-cc-pVTZ  | 1.1254 | 2.2932 | 89.81 | 1948.49 | 276.31 | 195.97 | -34.89 |
|        | MIN2      | aug-cc-pVTZ  | 1.1367 | 1.9357 | 117.64 | 1924.33 | 344.76 | 222.14 | -30.74 |

$^*$$^*$CASPT2(17,12) G2 energies, geometries, and harmonic vibrational frequencies derived from a grid of points by using the SURVIBTM program (Ref. 33).

$^*$$^b$Harmonic frequencies: $\omega_1$ (NO str, $a'$), $\omega_2$ (NOO bend, $a'$), and $\omega_3$ (OO str, $a'$), respectively. Masses of the most abundant isotopes were used: $^{14}$N and $^{16}$O.

$^*$$^c$Energy barrier respect to N($^4$S) + O$_2$.

$^*$$^d$Reference 22.
where their coefficients are also reported. For this minimum we have also performed calculations using the full valence active space \((17,12)\), and we have seen that increasing the size of the basis set slightly decreases the bond lengths. The geometry optimized at the CASPT2 level is very close to the CASSCF one, with the main difference being observed in the OO distance, which is shorter at the CASPT2 level. As a consequence of this OO shortening the OO stretching frequency is higher at the CASPT2 level compared to the CASSCF one.

From this peroxy minimum two TSs (i.e., TS2 and TS3) with almost no energy barrier over MIN1 lead directly to products \(O(3^1P) + NO\) (direct mechanism) or to another shallow minimum (MIN2), respectively. In spite of the good fit obtained for the \textit{ab initio} points grids around MIN1 and TS2 (i.e., a root-mean-square deviation below \(5 \times 10^{-3}\) \(\text{kcal/mol}\)), as their energies at the CASPT2 level are very close, their crossings and conical intersections, is under study in our group. The importance of the indirect \(C_s\)-insertion mechanism has been observed in a recent wave packet time-dependent quantum dynamics study\(^{51}\) by using our previous \(2A\)\(^1\) PES.\(^{10}\) Although this analytical PES does not properly reproduce the \(NO_2\) geometry \([\text{a linear } D_{\infty h} \text{ minimum is present at } -151.3 \text{ kcal/mol} \text{ respect to } O(3^1P) + NO]\) and fits and estimated energy barrier for the \(C_{2v}\) approach \([\text{i.e., } 47.46 \text{ kcal/mol respect to } N(4^3S) + O_2]\), it presents similar stationary points to the present MIN2 and TS4, which allow the access to the deep linear minimum. This produces a particularly high contribution of the \(C_s\)-insertion mechanism and a decrease in the overall reactivity. The importance of the \(C_s\)-insertion mechanism has also been observed by us in a preliminary QCT study using a new analytical PES based in the present \textit{ab initio} data.

The \(NO_2\) molecule does not present a potential energy barrier for the ground state dissociation \([\text{i.e., } O(3^1P) + NO]\) in agreement with preceding \textit{ab initio} studies of its photodissociation\(^{52}\) or unimolecular dissociation.\(^{45}\)

C. Characterization of the lowest \(4A\)\(^1\) potential energy surface

The geometries, harmonic vibrational frequencies, and energies relative to reactants, \(N(4^3S) + O_2\), for all the stationary points characterized at the \textit{ab initio} \([\text{i.e., CASSCF and CASPT2}]\) and DFT \([\text{i.e., UB3LYP}]\) levels for the lowest quartet PES are shown in Tables VI and VII. Figure 2 depicts the MERP connecting reactants and products, which is much simpler than for the doublet PES. All stationary points display \(C_{2v}\) symmetry. The highest energy barrier corresponds to TS1\(^{1'}\), whose values are compared in Table VI. CASSCF calculations with different basis sets and the lower active space \((11,9)\) provide resembling geometries, frequencies, and energy barriers.

The increase in the active space to \((17,12)\) produces a significant enlargement of the NO distance \((\text{ca., } 0.020 \text{ Å})\) and a little energy barrier decrease. The introduction of the dynamical correlation energy through the CASPT2 method \([\text{std or } G2]\) originates a large decrease in the energy barrier. The numerical optimization at the CASPT2\((17,12)\) G2 level gives a geometry \((\text{Table VI})\) for TS1\(^{1'}\) with a much longer NO distance \((\text{i.e., } 1.7803 \text{ Å})\) and a shorter OO distance \((\text{i.e., } 1.2559 \text{ Å})\). An energy barrier of 12.74 kcal/mol \((12.79 \text{ kcal/mol including ZPE differences})\) is obtained at the CASPT2\((17,12)\) G2/aug-cc-pVTZ level. The estimated CASPT2\((17,12)\) CBS limits for this energy barrier were \((a)\) 13.06 and 12.82 kcal/mol at the G2 level and \((b)\) 14.38 and 13.80 kcal/mol at the std. level, for cc-pVnZ and aug-cc-pVnZ series, with a maximum error of \(\pm 0.3 \text{ kcal/mol}\), estimated by using other exponential functions. The main difference in both CBS limits \((\text{ca. } 1.6 \text{ kcal/mol})\) arises again from

\[
0.917 \cdot (4a^2)^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(11a')^2(12a')^2(1a''')^2(2a'')^2(3a'')^0,
-0.222 \cdot (4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(11a')^2(12a')^2(1a')^0(2a'')^0(3a'')^2,
0.108 \cdot (4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(11a')^2(12a')^0(1a'')^0(2a'')^0(3a''')^1,
\]
the use of the G2 or standard CASPT2 variants, as it happens
including ZPE differences

| Method          | Basis set | $E$/a.u. | $R_{\text{NO}}$/Å | $R_{\text{NOO}}$/Å | $\omega_1$/cm$^{-1}$ | $\Delta E^\text{e}$/kcal mol$^{-1}$ |
|-----------------|-----------|----------|-------------------|---------------------|-----------------------|----------------------------------|
| CASSCF(11,9)    | ANO-A     | -204.118 630 | 1.6775 | 1.2740 | 107.02 | 637.62 | 428.23 | 1153.66 | 27.95 (28.0) |
|                 | cc-pVDZ   | -204.050 250 | 1.6554 | 1.2889 | 106.04 | 638.95 | 434.76 | 1094.41 | 29.50 (29.4) |
|                 | cc-pVTZ   | -204.104 769 | 1.6779 | 1.2750 | 106.81 | 644.14 | 426.93 | 1154.05 | 28.00 (28.05) |
|                 | cc-pVQZ   | -204.119 088 | 1.6793 | 1.2712 | 106.98 | 643.04 | 428.40 | 1165.84 | 27.89 (27.95) |
| aug-cc-pVDZ     | -204.064 530 | 1.6737 | 1.2785 | 106.21 | 650.45 | 413.76 | 1308.07 | 27.94 (28.18) |
| aug-cc-pVTZ     | -204.107 672 | 1.6628 | 1.2733 | 107.02 | 647.97 | 413.61 | 1311.54 | 27.53 (27.79) |
| CASPT2(11,9) std| cc-pVDZ   | -204.419 042 | | | | | | | | |
|                 | cc-pVTZ   | -204.633 391 | | | | | | | | |
|                 | cc-pVQZ   | -204.744 755 | | | | | | | | |
| aug-cc-pVDZ     | -204.466 923 | | | | | | | | |
| aug-cc-pVTZ     | -204.654 803 | | | | | | | | |
| CASPT2(11,9) G2 | cc-pVDZ   | -204.412 745 | | | | | | | | |
|                 | cc-pVTZ   | -204.625 376 | | | | | | | | |
|                 | cc-pVQZ   | -204.736 094 | | | | | | | | |
| aug-cc-pVDZ     | -204.459 359 | | | | | | | | |
| aug-cc-pVTZ     | -204.646 043 | | | | | | | | |
| CASPT2(17,12)   | ANO-A     | -204.127 828 | | | | | | | | |
|                 | cc-pVDZ   | -204.059 758 | | | | | | | | |
|                 | cc-pVTZ   | -204.113 893 | | | | | | | | |
|                 | cc-pVQZ   | -204.128 258 | | | | | | | | |
| aug-cc-pVDZ     | -204.073 784 | | | | | | | | |
| aug-cc-pVTZ     | -204.116 817 | | | | | | | | |
| CASPT2(17,12) std| cc-pVDZ   | -204.420 994 | | | | | | | | |
|                 | cc-pVTZ   | -204.633 745 | | | | | | | | |
|                 | cc-pVQZ   | -204.746 022 | | | | | | | | |
| aug-cc-pVDZ     | -204.468 858 | | | | | | | | |
| aug-cc-pVTZ     | -204.656 206 | | | | | | | | |
| CASPT2(17,12) G2 | ANO-A     | -204.608 718 | | | | | | | | |
|                 | cc-pVDZ   | -204.413 876 | | | | | | | | |
|                 | cc-pVTZ   | -204.625 855 | | | | | | | | |
|                 | cc-pVQZ   | -204.736 420 | | | | | | | | |
| aug-cc-pVDZ     | -204.460 319 | | | | | | | | |
| aug-cc-pVTZ     | -204.646 475 | | | | | | | | |
| CASPT2(17,12) G2 | aug-cc-pVTZ | -204.646 467 | 1.7803 | 1.2559 | 105.65 | 417.71 | 355.42 | 1260.84 | 12.74 (12.79) |
| UB3LYP          | aug-cc-pVTZ | 1.9206 | 1.2218 | 111.29 | 406.55 | 328.96 | 1428.27 | 14.18 (14.38) |
| CASCF(11,9)‡   | Dujneveldt | [11x6p/5s3p2d1f] | 1.669 | 1.288 | 109.9 | 612 | 365 | 1187 | 27.1 (27.1) |
| MR–CCI+Q/CASSCF(11,9)‡| Dujneveldt | [11x6p/5s3p2d1f] | 1.752 | 1.248 | 109.4 | 689 | 367 | 1406 | 18.0 (18.3) |

*CASPT2 energies at the CASSCF optimum geometries with the same basis set.

Primary basis set: [4a1g9p4d3f/4a1g3p2d1f] (Ref. 36).

Harmonic vibrational frequencies: $\omega_1$ (NO str, $a'$), $\omega_2$ (NOO bend, $a'$), and $\omega_3$ (OO str, $a'$), respectively. Masses of the most abundant isotopes were used: $^{15}$N and $^{16}$O.

Energy barrier with respect to $^{15}$N+$^{16}$O. The value corrected with the difference of zero point energies is shown in parentheses.

CASPT2 G2 optimum geometries and harmonic vibrational frequencies obtained by using the SURVIBTM program (Ref. 33).

Reference 18.

The use of the G2 or standard CASPT2 variants, as it happens

The present energy barriers are somewhat lower than the energy barrier fitted in a previous analytical quartet PES (Ref. 35) (i.e., 15.0 kcal/mol) based on MR–CCI+Q/CASSCF(11,9)/[11x6p/5s3p2d1f] calculations, which presented a virtual energy of 18.0 kcal/mol but with a very similar geometry to the CASPT2(17,12) G2 one (Table VI). We have also calculated the TS1’ energy barrier using the MR–CI+Q/aug-cc-pVTZ method with 11 electrons correlated (N and O 1s and 2s electrons were kept frozen), as for the doublet PES to compare with previous ab initio data. An energy barrier of 15.51 kcal/mol was determined by using a MR–CI calculation with 12 CSFs of reference, which is very close to the mentioned published data. CASPT2(11,9) G2 calculations without 2s electron correlation increases the barrier to 16.07 kcal/mol, which is very similar to the aforementioned MR–CI+Q value. Therefore, the 2s electron correlation becomes very important in both the CASPT2 and MR–CI calculations to calculate the energy barrier for both doublet and quartet PESs. The lower energy barrier found for the TS1’ in the quartet PES respect previous published data will produce larger thermal rate constants at high temperatures, where this excited PES becomes quite important (e.g., at 1500 K the $k_i$($^4$A’) contributes around a 10% of the total rate constant).

DFT calculations at the UB3LYP/aug-cc-pVTZ level provide a too long NO distances (i.e., 1.9206 Å) although a similar energy barrier of 14.18 kcal/mol (14.38 kcal/mol including ZPE differences). Some spin contamination was also
observed in TS1 (S^2) was 4.20 to be compared with the correct expectation value of 3.75.

TS1' leads to a very shallow minimum (MIN1') with a structure comparable to the peroxy minimum in the doublet PES. This minimum dissociates to O(3 P) + NO products through TS3', which has an energy barrier (7.81 kcal/mol) below that of TS1'. Hence, only a direct microscopic mechanism is expected for this PES differing from the double mechanism proposed for the doublet PES. DFT calculations at the UB3LYP/aug-cc-pVTZ level exactly corroborate the \textit{ab initio} MERP.

IV. CONCLUSIONS AND REMARKS

This work presents a detailed theoretical study of the N(4 S) + O_2 (X^3Σ^-) \rightarrow NO(X^2II) + O(3 P) exothermic reaction on its lowest ^2A' and ^3A' potential energy surfaces. \textit{Ab initio} CASSCF, CASPT2, and MR–CI methods with standard correlation-consistent (cc-pVnZ and aug-cc-pVnZ, n=D, T, Q, 5) Dunning’s basis sets and small and large atomic natural orbital basis sets were used; CBS limits were also reported for the main energy barriers (TS1 and TS1'). DFT methods were also used to facilitate the search of the stationary points, producing similar results too. Thus, several minima and transition states have been found along the different MERPs connecting reactants and products on both surfaces.

The ground ^2A' PES presents an average energy barrier (TS1) of 4.8 kcal/mol and 5.8 kcal/mol in the CBS limits for the G2 and std CASPT2 levels, respectively. The second value is almost coincident with the energy barrier (6.2 kcal/mol) derived from thermal rate constants in our previous paper. A peroxy NOO minimum is found in agreement with preceding \textit{ab initio} works, which seems to play an important role in the opening of a double microscopic reaction mechanism: direct C_s-abstraction and indirect C_s-insertion. The importance of this second mechanism through the NO_2 molecule has been recently anticipated in a wave packet time-dependent quantum dynamics study on our previous analytical doublet PES and also in our preliminary QCT study.

The alternative C_s-insertion mechanism with the different PESs and their crossings and conical intersections is currently under study in our group.

The ground ^2A' PES presents an average energy barrier (TS1') of 12.9 kcal/mol and 14.1 kcal/mol in the CBS limits for the G2 and std CASPT2 levels, respectively. In this surface another peroxy minimum is found, although in this case only a direct C_s-abstraction mechanism should be expected.

The present results improve previous high quality \textit{ab initio} studies and provide lower energy barriers for both PESs, which would produce larger values of both thermal rate constants, and therefore a larger total rate constant, with an expected better agreement with the available experimental data.

The good results obtained for reactants and products as well as for the peroxy NOO(^2A') minimum and for the NO_2(X^2A_1) molecule point towards the suitability of describing both PESs at the CASPT2(17,12) level of theory. Thus, two analytical PESs (^2A' and ^3A') based on several grids of \textit{ab initio} points have been almost fitted and dynamics and kinetics studies are currently in progress.

Finally, the study of the N and O 2s electron correlation in the MR–CI and CASPT2 methods shows that it is very important to correlate the 2s electrons, in both CASPT2 and MR–CI calculations, which produces lower energy barriers, much closer to the value estimated from experimental data. This point was not taken into account in previous \textit{ab initio} studies.

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