Formation of O_3^+ upon Ionization of O_2: The Role of Isomeric O_4^+ Complexes

Fulvio Cacace,*[a] Giulia de Petris,[a] Marzio Rosi,[b] and Anna Troiani[a]

Abstract: The course of the reaction of electronically and vibronically excited metastable $O_2^+(^4\Pi_u, \nu')$ ions with O_2, known to produce O_3^+, was examined by the joint application of computational and mass spectrometric methods. The results show that the reaction does not proceed by a direct mechanism and that it involves instead the intermediacy of the $[O_2^+(^4\Pi_u)\cdots O_2]$ and $[O_3^+(^4A_2)\cdots O]$ complexes, both theoretically characterized, and the latter one positively identified by structurally diagnostic mass spectrometric techniques. The reaction is a potential source of stratospheric ozone, in that O_3^+ ions are known to undergo efficient charge exchange with oxygen to yield neutral O_3.

Keywords: density functional calculations • gas-phase reactions • mass spectrometry • ozone

Introduction

The gas-phase reaction [Eq. (1)] is an example of a process, which is endothermic for the ground state of the reagents, but

$$O_2^+ + O_2 \longrightarrow O_3^+ + O \quad (1)$$

is known to occur when promoted by excited ions. Reaction (1) has long been studied using O_2^+ ions formed in excited states by electron ionization (EI)[1–6] and photoionization (PI)[7, 8] of O_2, and in experiments based on the molecular beam technique, which involves the PI of $(O_2)_n$ clusters.[9, 10] A related study, focused on the analysis of isotope effects, has utilized O_2^+ ions generated by EI ionization of O_2.[11] As a result of the above studies, it appears to be firmly established that reaction (1), promoted primarily by O_2^+ $(^4\Pi_u, \nu')$ ions interacting with ground-state O_2 $(^3\Sigma_g^+)$ molecules, displays a threshold at $\nu' \geq 5$ and the highest efficiency at $\nu' = 9$. In addition to this fundamental piece of information, no detailed mechanistic studies of reaction (1) have been reported. No information is available on the role of its conceivable intermediates, that is, some O_4^+ complexes, nor has it been established whether ionization of O_2 can represent an ionic route to *neutral* ozone, a process potentially relevant to atmospheric chemistry, especially in view of the debated question of the *ozone deficit*.[12] In this study, motivated by our interest in oxygen allotropes and simple species relevant to the chemistry of the atmosphere, such as O_4, HO_3, $[H_2O^+ O_2^-]$, and so on,[13] we examine the mechanism of process (1) by the joint application of theoretical and mass spectrometric techniques.

Methods

The experimental approach utilized well-established mass spectrometric techniques, that is, electron (EI) and chemical ionization (CI) to generate the charged species of interest and collisionally activated dissociation (CAD) spectrometry for their structural characterization. Neutralization–reionization (NR) mass spectrometry[14] was used as an additional tool to gather further structural insight from the examination of the charged species from the reionization of the uncharged species obtained upon vertical neutralization of the ions probed.

As to the theoretical methods, density functional theory, using the hybrid B3LYP functional,[15] was used to localize the stationary points of the investigated systems and to evaluate the vibrational frequencies. Although it is well known that density functional methods using nonhybrid functionals sometimes tend to overestimate bond lengths, hybrid functionals as B3LYP usually provide geometrical parameters in excellent agreement with experiments.[16] Single-point-energy calculations at the optimized geometries were performed using the coupled-cluster single and double excitation meth-

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od[17] with a perturbational estimate of the triple excitations (CCSD(T) approach[18]) in order to include extensive correlation contributions.[19] Transition states were located using the synchronous transit-guided quasi-Newton method of Schlegel and co-workers.[20] The 6-311 + G(3df) basis set[21] was used. Zero-point-energy corrections evaluated at the B3LYP/6-311 + G(3df) level were added to the CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational, and vibrational contributions. The absolute entropies were calculated by using standard statistical – mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311 + G(3df) optimized geometries.

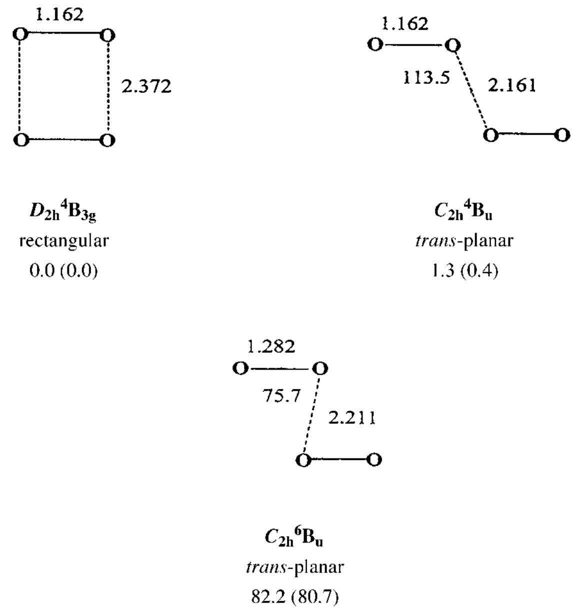
Selected geometry optimization was performed at the CCSD(T) level. Zero-point-energy corrections evaluated at the CCSD(T)/6-311 + G(3df) level were added to the CCSD(T) energies. The 0 K total energies of the species of interest were corrected to 298 K by adding translational, rotational, and vibrational contributions. In this case, the absolute entropies were calculated by using standard statistical – mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to CCSD(T)/6-311 + G(3df) optimized geometries. All calculations were performed using Gaussian 98.[22]

Results

Computational results: We focused our attention on the rectangular and *trans*-planar structures of O_4^+, that were previously computed to be the most stable ones.[23] Both the optimization of the geometry and the calculation of the vibrational frequencies were performed at CCSD(T) level in order to minimize the well-known symmetry-breaking effects.[24] The optimized geometries of O_4^+ are shown in Figure 1. The $^4B_{3g}$ state, corresponding to the rectangular structure, was computed to be slightly more stable than the ^4B_u state, corresponding to the *trans*-planar geometry, by 0.4 kcal mol^{-1} at 298 K. The binding energy of O_4^+ in its $^4B_{3g}$ ground state, computed with respect to O_2 ($^3\Sigma_g^-$) and O_2^+ ($^2\Pi_g$), is 8.9 kcal mol^{-1} at 298 K with inclusion of zero-point energy. This value is in very good agreement with the most recent experimental estimate of 9.15 ± 0.5 kcal mol^{-1},[23, 25, 26] and with the best computed value so far available, 11.0 kcal mol^{-1}.[23] The endothermicity of the formation of separated O_3^+($^2A_1$) and O(^{3}P) from O_4^+($^4B_{3g}$) is computed to be 113.9 kcal mol^{-1} at 298 K.

We performed calculations also on O_4^+ in its first excited sextet state. The optimized geometry of the ^6B_u state of O_4^+ is shown in Figure 1. The ΔH° change for the dissociation of O_4^+(^6B_u) into O_2 in its ground state ($^3\Sigma_g^-$) and O_2^+ in its first excited quartet state ($^4\Pi_u$) is computed to be 21.8 kcal mol^{-1} at the CCSD(T) level of theory. The energy of O_2^+ in the $^4\Pi_u$ state has been estimated taking into account the experimental separation between the ground and the first excited ^6B_u state of O_2^+.[29] The ^6B_u state of O_4^+ is computed to be 80.7 kcal mol^{-1} higher in energy with respect to the ground state at 298 K. This value suggests that the dissociation of O_4^+, even in its excited ^6B_u state, into O_3^+ and O(^{3}P) is still endothermic, and the computed ΔH° change of this reaction is 33.2 kcal mol^{-1} at 298 K. Therefore this reaction could occur only if O_4^+(^6B_u) is also vibrationally excited, in agreement with the evidence from experimental studies.[1–8]

In Figure 2 we report the geometries optimized at the B3LYP level of the minima localized in the quartet ground state and the sextet excited state potential energy surfaces of O_4^+. In Table 1 we report the ΔH° values at 298 K for selected reactions. We notice that these values are clearly overestimated at the B3LYP level. However, we can also notice that the CCSD(T) values are reasonable even when utilizing the B3LYP optimized geometries, which supports the idea of optimizing the geometries at the B3LYP level and computing the energetics at CCSD(T) level. Using the B3LYP method, we were able to localize the saddle points reported in Figure 3 for the dissociation of O_4^+ into O_3^+ + O both on the quartet and the sextet potential energy surfaces. Since the difference between the *cis* and *trans* isomers is small, we focused our attention on the *trans* isomer. On the quartet surface, the conversion of the O_4^+($^4B_{3g}$) complex into the $^4A''$ complex



D_{2h} $^4B_{3g}$
rectangular
0.0 (0.0)

C_{2h} ^4B_u
trans-planar
1.3 (0.4)

C_{2h} ^6B_u
trans-planar
82.2 (80.7)

Figure 1. Optimized CCSD(T) geometries and B3LYP energies [kcal mol^{-1}] of relevant O_4^+ species, see text. Data in parentheses include thermal correction at 298 K.

Abstract in Italian: *È noto che ioni metastabili O_2^+($^4\Pi_u$, v'), elettronicamente e vibrazionalmente eccitati, reagiscono con l'ossigeno producendo O_3^+. Il meccanismo della reazione è stato esaminato con una combinazione di metodi teorici e spettrometrici di massa. I risultati mostrano che non si tratta di una reazione diretta ma che, al contrario, essa procede attraverso due intermedi, i complessi [O_2^+($^4\Pi_u$) ··· O_2] e [O_3^+($^4A_2$) ··· O]. Entrambi sono stati caratterizzati dal punto di vista teorico ed il secondo è stato identificato con certezza mediante l'analisi della sua struttura con tecniche spettrometriche di massa. La reazione è una possibile fonte di ozono nella stratosfera, in quanto è noto che gli ioni O_3^+ scambiano efficacemente la carica con l'ossigeno, producendo O_3 neutro.*

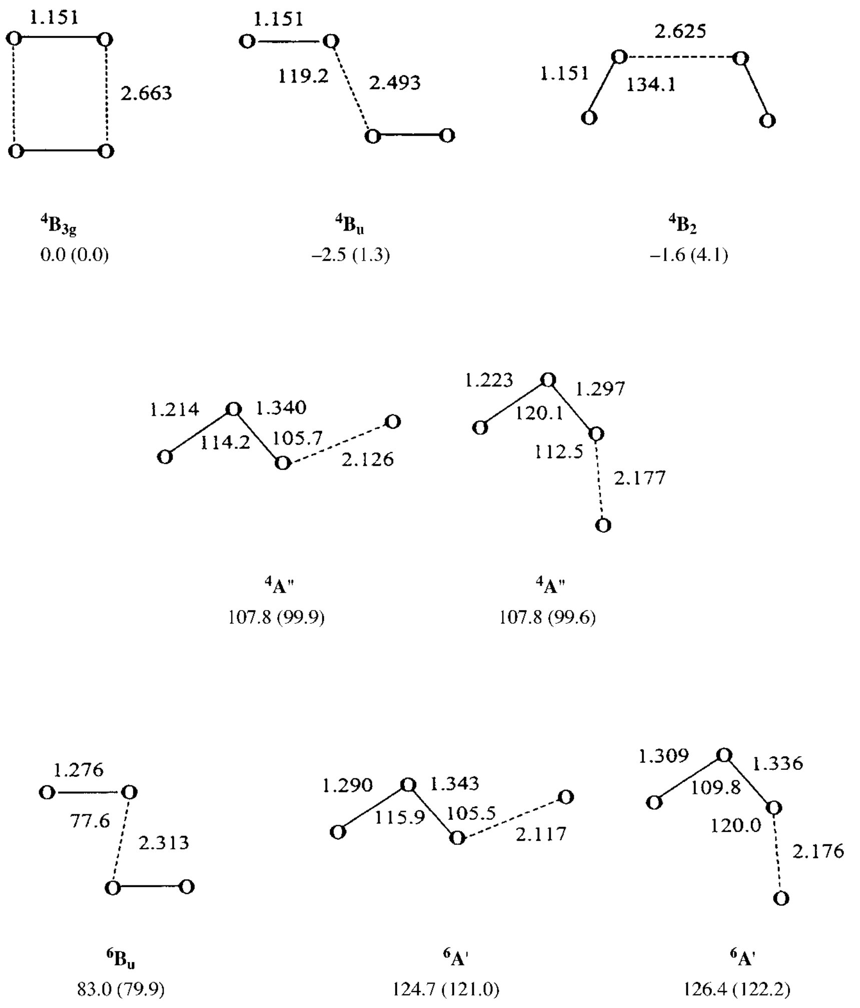


Figure 2. Optimized B3LYP geometries and energies of relevant O_4^+ species, see text. CCSD(T) energies in parentheses.

Table 1. Energy changes and barrier heights [kcal mol^{-1}, 298 K] computed at the B3LYP (CCSD(T)) level of theory for selected dissociation reactions.

Process	ΔH°	Barrier height
geometries optimized at CCSD(T) level		
O_4^+ ($^4B_{3g}$) → O_2^+ ($^2\Pi_g$) + O_2 ($^3\Sigma_g^+$)	(8.9)	
O_4^+ ($^4B_{3g}$) → O_3^+ ($^2A_1$) + O (^3P)	(113.9)	
O_4^+ (^6B_u) → O_2^+ ($^4\Pi_u$) + O_2 ($^3\Sigma_g^+$)	(21.8)	
geometries optimized at B3LYP level		
O_4^+ ($^4B_{3g}$) → O_2^+ ($^2\Pi_g$) + O_2 ($^3\Sigma_g^+$)	29.0 (7.5)	
O_4^+ ($^4B_{3g}$) → O_3^+ ($^2A_1$) + O (^3P)	136.7 (113.0)	
O_4^+ ($^4B_{3g}$) → [O_3^+ ··· O]($^4A''$)	107.8 (99.9)	111.2 (104.5)
[O_3^+ ··· O]($^4A''$) → O_3^+($^2A_1$) + O (^3P)	28.9 (13.1)	
O_4^+ (^6B_u) → O_2^+ ($^4\Pi_u$) + O_2 ($^3\Sigma_g^+$)	40.2 (21.8)	
O_4^+ (^6B_u) → [O_3^+ ··· O]($^6A'$)	41.7 (41.0)	50.6 (43.6)
[O_3^+ ··· O]($^6A'$) → O_3^+($^4A_2$) + O (^3P)	19.0 (15.6)	

formed by O_3^+($^2A_1$) and O(^3P) is computed to be endothermic by 99.9 kcal mol^{-1} and to have, in addition, a kinetic barrier of 4.6 kcal mol^{-1}, so that the TS is located 104.5 kcal mol^{-1} over the reagent. Dissociation of the $^4A''$ complex into O_3^+($^2A_1$) and O(^3P) is endothermic by 13.1 kcal mol^{-1}, also at the CCSD(T) level of theory.

Passing to the sextet surface, the conversion of the O_4^+(^6B_u) complex into the $^6A'$ complex formed by O_3^+($^4A_2$) and O(^3P) is computed to be endothermic by 41.0 kcal mol^{-1} at the CCSD(T) level of theory and to have a kinetic barrier of 2.6 kcal mol^{-1}, so that the TS state is located 43.6 kcal mol^{-1} above the reagent. Dissociation of the $^6A'$ complex into O_3^+($^4A_2$) and O(^3P) is endothermic by 15.6 kcal mol^{-1}, also at the CCSD(T) level of theory. Note that the O_3^+ cations from the $^4A''$ and the $^6A'$ complexes, namely from the reactions occurring on the quartet and the sextet surfaces, are in different electronic states, that is, the ground $^2A_1$ and the excited $^4A_2$ state, respectively.

Mass spectrometric results: The species of interest were produced by ionization of O_2 by 20 eV electrons, as suggested by previous results showing that O_3^+, the formation of which is promoted by O_2^+ ($^4\Pi_u$, ν'), has an appearance potential of 16.7 eV,[4] and its relative intensity levels off at approximately 20 eV.[11] In all cases, O_2^+ is by far the most abundant ion, accompanied by O_3^+ and O_4^+, the intensities of which depend on the O_2 pressure, as apparent

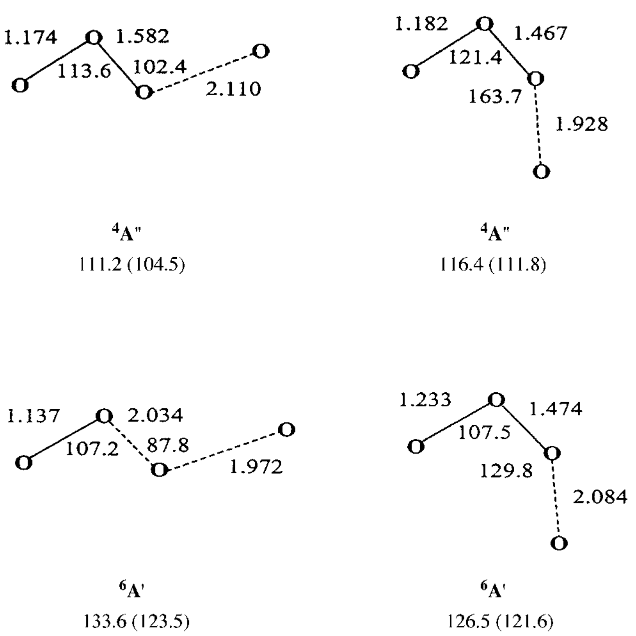


Figure 3. Optimized B3LYP geometries and energies of the saddle point for the dissociation of O_4^+ into O_3^+ + O, see text. CCSD(T) energies in parentheses.

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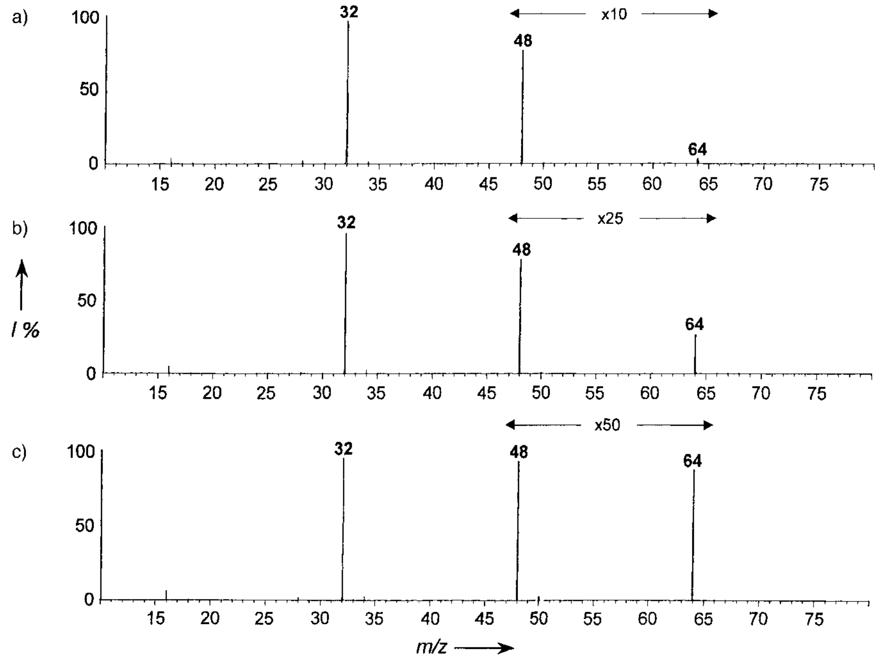


Figure 4. Relative intensities of the O_2^+, *m/z* 32, O_3^+, *m/z* 48, and O_4^+, *m/z* 64 from the ionization of oxygen by electrons of 20 eV nominal energy at various pressures, see text.

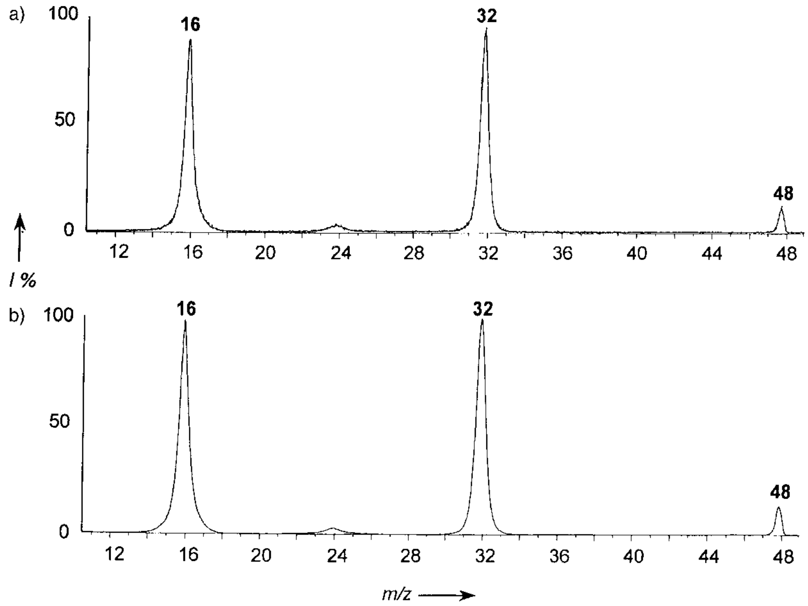


Figure 5. $^+NR^+$ spectra of the O_3^+ ions: a) from reaction (1); b) from the ionization of ozone.

from the typical spectra illustrated in Figure 4. Whereas the quantitative study of the pressure dependence of the ionic species formation is outside the scope of the present work, the pronounced decrease of the O_3^+ and O_4^+ intensities at lower pressures is clearly apparent on inspection of the spectra of Figures 4a–c, recorded at pressures of ≈0.1, 0.02, and 1×10^{-3} Torr, respectively. Structural analysis of the O_3^+ and O_4^+ populations was performed by CAD and NR mass spectrometry.[30] The structural features of the O_3^+ population from the ion source are unaffected by changes of the O_2 pressure, although its intensity decreases at low pressure. Based on its CAD and NR spectra, that correspond to those of O_3^+ from the ionization of O_3, the species probed can be assigned as the molecular cation of ozone; no evidence emerges for other conceivable isomers of *m/z* 48, for example, $[O_2 \cdots O^+]$ ion–molecule complexes, that would not be amenable to neutralization to the bound O_3 molecule observed in the NR experiments (Figure 5). By contrast, the CAD spectra of the O_4^+ populations denote the presence of isomeric ions, the proportions of which change with the pressure in the source. At the highest pressure, ≈0.1 Torr, the CAD spectrum displays only the O_2^+ fragment, which denotes a O_2-O_2 connectivity. A tenfold pressure decrease strongly reduces the O_4^+ intensity, whose CAD spectrum changes displaying, in addition to the O_2^+ fragment, also an O_3^+ fragment. These trends are enhanced by a further decrease of the pressure, to the point that O_3^+ becomes the major fragment at the lowest pressure investigated (Figure 6). The observed changes of the CAD spectra indicate the presence of an isomeric $[O_3^+-O]$ complex, the abundance of which increases as the pressure is lowered. Strong support for such an inference is provided by the results of the following MS^3 experiments. First, the O_4^+ ions, generated in the source in the low-pressure regime, were collisionally decomposed in a cell located in the second field free region (FFR), and the O_3^+ fragment obtained was then structurally analyzed in the cell located in the TOF mass spectrometer, and this gave a CAD spectrum indistinguishable from that of O_3^+ from the ionization of ozone (Figure 7a). Similar experiments were performed by using $O_2/^{18}O_2$ gaseous mixtures. The $O_2{}^{18}O_2^+$ ions thus obtained gave both the $O^{18}O_2^+$ and $O_2{}^{18}O^+$ fragments, the CAD-TOF spectra of which confirm the above result. Secondly, the O_4^+ ions from the source, operated at the same pressure, were dissociated by collision with He in a gas cell located in the first FFR, and the O_3^+ fragment obtained is mass/energy selected and neutralized in the cell pair located in the second FFR. The resulting NR spectrum corresponds to that of the model O_3^+ ion from the ionization of ozone (Figure 7b).

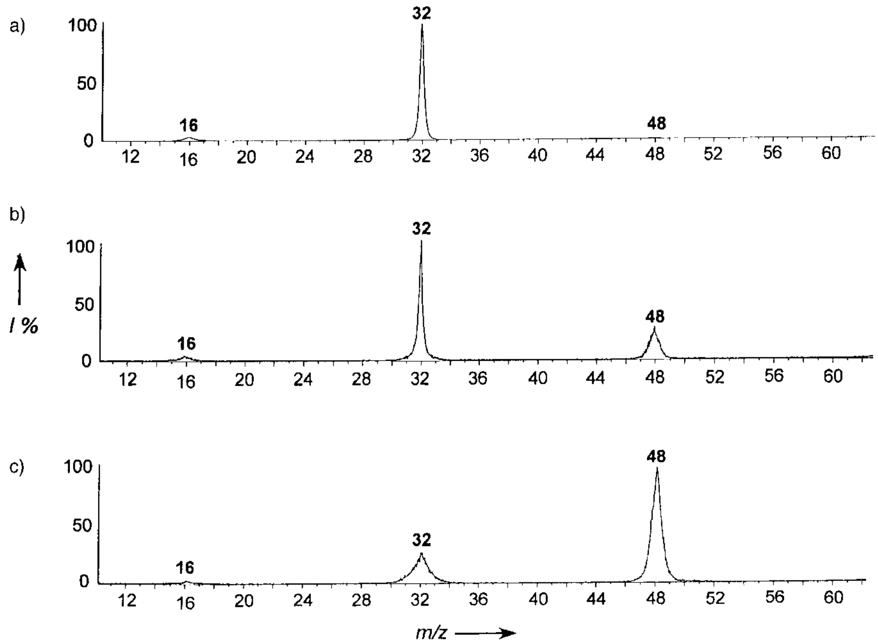


Figure 6. CAD spectra of O_4^+ ions formed at different pressures, see text.

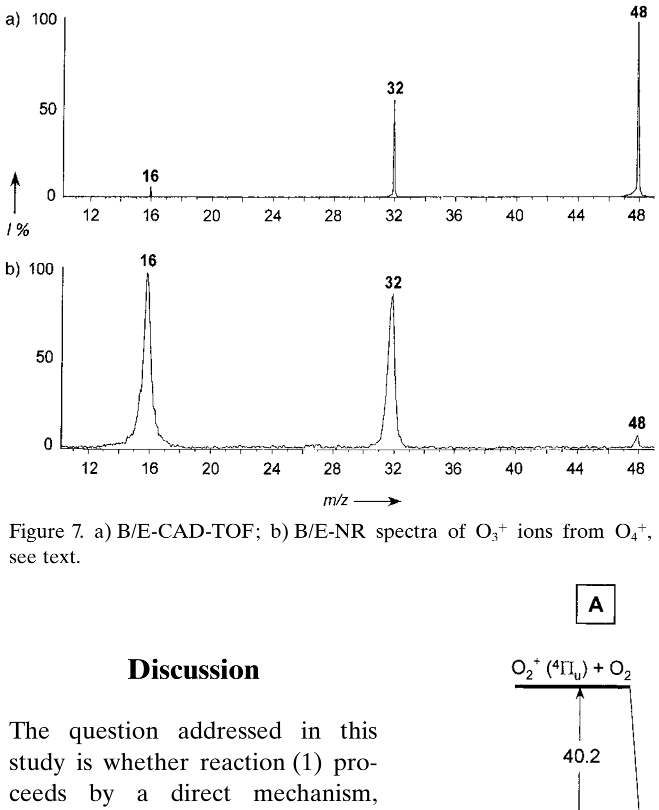


Figure 7. a) B/E-CAD-TOF; b) B/E-NR spectra of O_3^+ ions from O_4^+, see text.

Discussion

The question addressed in this study is whether reaction (1) proceeds by a direct mechanism, namely it is a fast process, promptly following the bimolecular collision of the reagents, or the ionization of $(O_2)_2$ van der Waals clusters, rather than a stepwise process involving intermediate O_4^+ complexes.

The theoretical analysis of the deceptively simple O_4^+ system is notoriously difficult, especially *when electronically excited species are involved*, owing to the problems arising from their multireferenced wave functions. This is clearly illustrated by the B3LYP and CCSD(T) energy profiles compared in Figures 8 and 9. Indeed, the latter method gives a ΔH° change of 8.9 kcal mol^{-1} for the association of ground-state O_2^+ ($^2\Pi_g$) and O_2 ($^3\Sigma_g^+$) into a ($^4B_{3g}$) ground-state [$O_2^+\cdots O_2$] complex, a result in excellent agreement with the experimental 9.2 kcal mol^{-1} value.[27, 28] Note that in this case ground-state species are involved. By contrast, the CCSD(T) ΔH° change, 34.8 kcal mol^{-1}, considerably exceeds the 9.9 kcal mol^{-1} value derived from the available thermochemical and spectroscopic data[31] for the process [Eq. (2)].

$$O_2^+\ (^4\Pi_u) + O_2\ (^3\Sigma_g^+) \longrightarrow O_3^+(^4A_2) + O(^3P) \qquad (2)$$

that involves electronically excited ions. The B3LYP ΔH° change, 20.5 kcal mol^{-1}, is closer to the experimentally derived value, but the method considerably overestimates the stability of O_4^+ complexes, as apparent from the ΔH° change computed for the dissociation of the ($^4B_{3g}$) ground-state [$O_2^+\cdots O_2$] complex into the monomers, namely 29.0 kcal mol^{-1}, a result that largely exceeds both the CCSD(T) and the experimental values.

The theoretical analysis is nevertheless useful in order to evaluate the mechanistic role of intermediate O_4^+ complexes in reaction (1). First, both theoretical methods (see complex **1** and complex **2**)

[$O_2^+(^2\Pi_g)\cdots O_2\ (^3\Sigma_g^+)$] **1** ($^4B_{3g}$)

[$O_2^+\ (a^4\Pi_u)\cdots O_2(^3\Sigma_g^+)$] **2** ($^6B_u$)

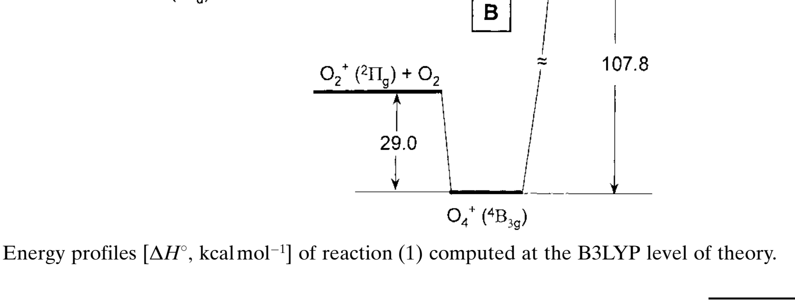


Figure 8. Energy profiles [ΔH°, kcal mol^{-1}] of reaction (1) computed at the B3LYP level of theory.

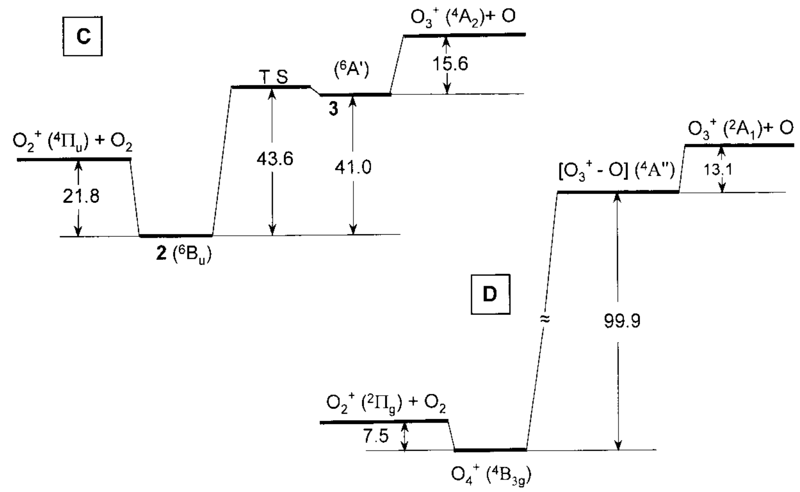


Figure 9. Energy profiles of reaction (1) computed at the CCSD(T) level of theory.

point to the considerably higher stability of complex **2** relative to that of complex **1**, consistent with the higher clustering ability of the excited $O_2^+(^4\Pi_u)$ ion than of the ground-state O_2^+ ($^2\Pi_g$) ion, established by previous experimental results.[11] Even more important, both theoretical methods predict that complex **3** is sufficiently

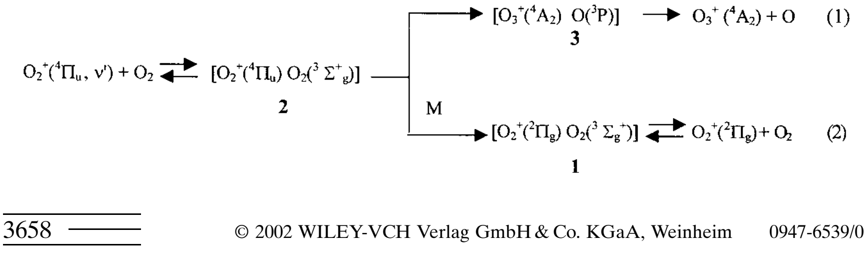
$$[O_3^+\cdots O] \quad \mathbf{3}\ (^6A') \qquad (3)$$

stable to allow its detection, since the ΔH° change for its dissociation into O_3^+ ($^4A_2$) and O(^{3}P) is computed to range from 15.6 to 19.0 kcal mol^{-1}, a prediction fully consistent with the experimental results reported in the previous section.

By combining the theoretical results with the mass spectrometric evidence on the nature, the abundance, and the structure of the charged species formed upon ionization of O_2, one can derive a consistent mechanistic picture of reaction (1) that points to the role of intermediate O_4^+ complexes. Ionization of O_2 by 20 eV electrons is known to yield vibronically excited O_2^+ ($^4\Pi_u$, ν') ions, together with ground-state $O_2^+(^2\Pi_g)$ ions.[11] The radiative lifetime of the O_2^+ excited ions, over 1 ms,[31, 32] exceeds the mean time between collisions within the source in the pressure range of interest. Hence, those electronically excited ions that contain, in addition, excess vibrational energy ($\nu' \geq 5$) can promote the following reaction sequence.

It can be noted that the reaction channel (2) is tantamount to collisional relaxation of the metastable $O_2^+(^4\Pi_u)$ ions to ground-state O_2^+ ions, that, in addition to those directly formed in the primary ionization, can reversibly associate with O_2 molecules yielding the ground-state ($^4B_{3g}$) complex **1**.

The above scheme, that rests heavily on the experimental results, accounts for the nature of the charged species leaving the source, that is, the O_2^+, O_3^+, and O_4^+ cations, and for the dependence of their relative intensity on the source pressure. Indeed, the relatively weakly bound complex **1** is expected to undergo increasing dissociation as the pressure is lowered. The same applies to complex **2**, and hence to its product O_3^+, consistent with the experimentally observed trend. Passing to the structural analysis of the ionic populations, the paramount experimental result is the compelling evidence, in particular from the CAD-TOF and B/E-NR spectra of O_4^+, showing that the O_3^+ fragment, to be assigned as ionized ozone, is formed from the dissociation of the particular O_4^+ isomer that becomes predominant in the low-pressure range. Hence, this isomer is characterized as the $[O_3^+\cdots O]$ complex **3**, which establishes its intermediacy in process (1).



The presence of the other intermediate, complex **2**, cannot be experimentally demonstrated, since its CAD spectrum would be indistinguishable from that of complex **1**, which is characterized by the same $O_2\cdots O_2$ connectivity. Moreover, it is doubtful whether **2** can be present at all in the population of O_4^+ ions that exit from the source. Indeed, albeit radiatively long-lived, $O_2^+(^4\Pi_u)$ ions are known to undergo fast relaxation to ground-state $O_2^+(^2\Pi_g)$ ions upon collision with O_2. The relaxation rate is unlikely to be significantly affected by the perturbation of the $O_2^+(^4\Pi_u)$ ion caused by relatively weak interaction with the O_2 molecule in complex **2**. As a consequence, unless **2** undergoes fast intracomplex conversion into **3** by overcoming the relative barrier, it is bound to be collisionally quenched to **1** before leaving the source, which is very likely the fate of the fraction of complexes formed by $O_2^+(^4\Pi_u, \nu')$ in its lower vibrational levels ($\nu' < 5$).

Conclusion

The results of the present study support a mechanistic interpretation of reaction (1) involving the intermediacy of the O_4^+ isomeric complexes **2** and **3**. Both have been theoretically characterized, and the latter one positively identified by molecular mass, elemental composition, and structural analysis by several mass spectrometric techniques. Reaction (1) is of potential interest to atmospheric chemistry as an ionic route to ozone in the stratosphere, especially since a previous ICR study has shown that O_3^+ undergoes efficient charge exchange with oxygen to yield *neutral* O_3.[33]

Experimental Section

The experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration, where E and B stand for electric and magnetic sectors, and TOF for orthogonal time-of-flight mass spectrometer. The instrument was fitted with EI and CI ion sources, a gas cell located in the first field free region, and two pairs of gas-collision cells located after the magnet along the beam path. Typical operating conditions of the CI source were as follows: source temperature: 373 K; repeller voltage: 0 V; emission current: 1 mA; nominal electron energy: 20 eV. Typical EI source conditions were: source temperature: 373 K; trap current: 200 μA; electron energy: 20 eV. The ions from the source were accelerated to 8 kV, and their CAD and NR spectra recorded by utilizing the first of the collision cell pair, located between the magnet and the second E sector. The target gas utilized in the CAD experiments was He, admitted into the first cell at a pressure adjusted to achieve a 80% transmittance. In the NR experiments CH_4, used as the neutralizing gas, was also admitted into the first of the cell pair at such a pressure to achieve a beam transmittance of 80%. All ions were then removed by a pair of high voltage (1 kV) deflecting electrodes, and the beam of fast neutral species entered the second cell, in which reionization was achieved utilizing O_2 as the stationary collider. The NR spectra were averaged over 100 acquisitions to improve the signal-to-noise ratio. The following MS^3 (multistage mass spectrometry) experiments were performed: i) the selected precursor ion underwent decomposition by collision with He in the first of the cell pairs located in the second field free region, and an energy-selected daughter ion was structurally analyzed by CAD-TOF in the cell located in the TOF mass spectrometer; ii) the selected precursor ion underwent decomposition by collision with He in the cell located in the first field free region and a daughter ion, mass/energy-selected by a linked scan, was subjected to NR in the cell pair located in the second field free region (B/E-NR mass spectrometry).

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