News about Oxygen

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Within the last decade, rapid improvements in the development of quantum chemical methods as well as computers have enabled theoreticians to pose several provocative questions to experimentalists engaged in the chemistry of oxygen.

> *“Is there a transition state for the unimolecular dissociation of cyclotetraoxygen (O_4)?”*[1]
> *“Can oxywater be made?”*[2]
> *“How long can you make an oxygen chain?”*[3]

Meanwhile, some of these, as well as several related aspects of neutral H_mO_n compounds ($m = 0-2$, $n = 2-4$), have been addressed experimentally using neutralization–reionization (NR) mass spectrometry.[4, 5] The NR method starts with the generation of the corresponding ionic species, which are then accelerated to kinetic energies of several keV, mass selected, and neutralized by vertical electron transfer (ET) in a high-energy collision. After removal of all ionic species, the remaining, still fast-moving neutrals are reionized in another keV collision, mass-analyzed, and detected (Figure 1). The NR method typically samples neutrals having lifetimes within or exceeding the μs regime. While this interval appears to be rather short, it is in fact almost an eternity for small systems such as the H_mO_n species considered here because the entire rovibrational manifold, which includes formally spin-forbidden reactions, can exhaustively be explored in this period.[6]

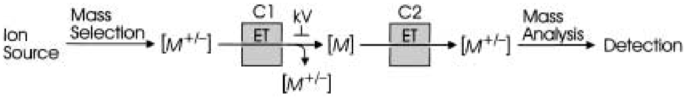
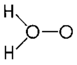


Figure 1. Schematic representation of an NR experiment.[4, 5] A mass-selected beam of cationic or anionic projectiles $M^{+/-}$ generated in the ion source is neutralized in a first collisional ET in the collision cell C1. Subsequently, all the charged species are deflected by a kV voltage leaving a beam of fast-moving neutrals which enters a second collision cell C2 where reionization by a second ET takes place. The ionic species formed are then mass analyzed and detected by conventional mass spectrometric means.

After the NR method had been successfully applied for the detection of the elusive oxywater **1**[7] the group of Cacace at the University of Rome systematically investigated oxygen chemistry, and several H_mO_n species have been shown to exist as long-lived neutrals in the gas phase.[8–10] Parallel work of Speranza and co-workers from the very same faculty has provided valuable energetic information about species such as **2**–**4**.[11, 12] For example, the $HO_3^{\bullet}$ radical **2**, has repeatedly been postulated as an important intermediate in atmospheric processes, although it has never been detected experimentally. In particular, it was not clear whether the combination of atomic hydrogen with ozone might lead to a long-lived $HO_3^{\bullet}$ radical or if immediate dissociation into O_2 and $HO^{\bullet}$ takes place. In 1999, NR experiments conducted by Cacace et al. with mass-selected HO_3^+ ions generated from protonated ozone, proved the existence of the neutral $HO_3^{\bullet}$ radical in the μs range,[9] thereby corroborating the need for the inclusion of this species in the modeling of the atmospheric chemistry of ozone.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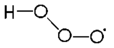
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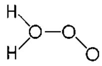
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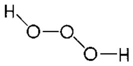
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The particular stimulus for this Highlight is the recent detection of a long-lived O_4 species by the Cacace group.[13] The interest in oxygen modifications other than O_2 and O_3 has two facets. On the one hand, formation of transient O_4 has been postulated to affect the ozone concentrations in the lower stratosphere by reactions with atomic oxygen [Eq. (1)].[14] On the other hand, higher oligomers of oxygen O_n ($n = 4, 6, 8, 12$) have been investigated theoretically in the search for high-energy dense materials (HEDM) to be used as possible rocket propellants or explosives. For example, cyclic O_8 has been predicted by theory to exist as a high-energy modification of oxygen in analogy to cyclooctasulfur S_8, and O_8 can indeed be considered as an HEDM because dissociation into four O_2 molecules is predicted to be exothermic by about 95 kcal mol^{-1}.[15] As far as the O_4 molecule is concerned, the various theoretical predictions made so far are somewhat divergent. The spread of the theoretical results is not at all unexpected, however, because a molecule such as O_4 imposes

$$O + O_3 \rightarrow [O_4] \rightarrow 2\,O_2 \qquad (1)$$

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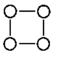
extreme demands to the description of electron correlation, symmetry breaking as well as significant multi-reference character of the wavefunctions is to be expected, and finally, spin–orbit coupling must be included in a proper assessment of the kinetic stability of O_4. The most recent study does indeed suggest that the singlet state of cyclotetraoxygen is kinetically stabilized by a barrier of about 6 kcal mol^{-1} with respect to the very exothermic dissociation into two (triplet) O_2 molecules.[16]

The NR experiments of Cacace et al.[13] have now established unambiguously that neutral O_4 can exist as a transient in the µs regime. To this end, chemical ionization (CI) of dioxygen was used to generate $O_4^{+\bullet}$ radical cations[17] which were then mass-selected and subjected to a NR sequence. Distinct recovery signals, clearly arising from neutral O_4, were observed for all isotopic combinations examined in these NR experiments. The flip side of the coin is, however, that the various experimental findings were incompatible with the theoretical predictions for the covalent O_4 species considered so far. At first, isotopic labeling disfavors the cyclic structure **5** of the neutral O_4 transient because the NR spectrum of $^{16}O_2{}^{18}O_2^{+\bullet}$ (formed by CI of a $^{16}O_2/^{18}O_2$ mixture) gives rise to $^{16}O_2^{+\bullet}$ and $^{18}O_2^{+\bullet}$ fragments in almost equal abundancies, but very little $^{16}O^{18}O^{+\bullet}$. However, a 1:2:1 ratio of $^{16}O_2^{+\bullet}$, $^{16}O^{18}O^{+\bullet}$, and $^{18}O_2^{+\bullet}$ is expected for a cyclic structure, and similar arguments apply to a possible pinwheel structure **6** ("ozone oxide"). In turn, generation of a mere van der Waals complex **7** also appears improbable, because the NR experiments proceed as a sequence of vertical ET steps in high-energy collisions which is rather unlikely to be survived by the $[O_2 \cdot O_2]$ van der Waals complex, which has a binding energy of less than 1 kcal mol^{-1}.[18] While the experimental results might be explained by invoking an acyclic, covalently bound O_4 isomer, none of the previous theoretical studies gives any indication that such a species is stable. Hence, we arrive at a situation where the result of the NR study itself is unambiguous in that transient neutral O_4 exists, while the nature of the species formed remains unknown.[19] Cacace et al.[13] suggest the formation of a bound molecule, formally described as $[O_2^* \cdot O_2]$ (**8**) which arises from excited states of dioxygen which themselves have also been suggested to participate in atmospheric processes such as the ozone cycle and terrestrial and venusian nightglows.[20]



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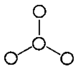

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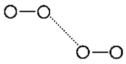

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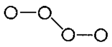

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Even more than 200 years after the "discovery" of oxygen,[21] speculation about new modifications of oxygen is not restricted to the peculiar conditions of the idealized gas phase. In an entirely different context, a group of Italian physicists has recently provided independent evidence for the existence of O_4 in the ε-phase of solid oxygen formed at high pressures.[22] Further, a group at the Lawrence Livermoore National Laboratory (USA) presented evidence for the existence of metallic modifications of oxygen at very large pressures of up to 2 Mbar.[23, 24]

Notwithstanding these new experimental observations, an extension to a preparative scale, or an isolation of O_4, cannot be foreseen. Hence, theoretical assistance is needed again in the search for new O_4 molecules which exhibit lifetimes in the µs regime (or more) and are likely to survive a sequence of keV collisions occurring in NR experiments. In other words, the ball thrown out by theoreticians bounces back to them once more. Let us await whether or not the next round can provide more definitive information about the existence and identity of new allotropes of oxygen.

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Note added in proof: Recently Cacace et al. also obtained experimental proof of tetranitrogen: F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480.