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Experimental Detection of Tetraoxygen[**]

Fulvio Cacace,[*] Giulia de Petris, and Anna Troiani

The search for tetraoxygen, which dates back to a study by Lewis in 1924,[1] is being actively pursued, owing to its fundamental interest, its potential role as a material of high energy density,[2] and, in particular, the current upsurge of interest in excited states of O_2 with relevance to atmospheric chemistry and to terrestrial and Venusian nightglow.[3] Numerous calculations at different levels of theory predict the existence of metastable O_4 molecules with a D_{2d} cyclic geometry[4] or a D_{3h} "pinwheel" geometry.[5, 6] Positive experimental detection of such species has not been reported, whereas weakly bonded $(O_2)_2$ van der Waals dimers, with dissociation enthalpies of less than 1 kcal mol^{-1}, have long been known and thoroughly characterized.[7] Indirect evidence for metastable tetraoxygen was derived from experiments involving electron transfer from Cs to O_4^+, followed by the measurement of the kinetic energy spectrum of the O_2 fragments. The structure of the kinetic energy distribution was consistent with the intervention of some O_4 species that were not observable under the conditions of the experiment.[8] Strong evidence for metastable O_4 was derived from studies involving the photoionization of O_2 excited by a DC discharge.[9, 10] Interestingly, the results of both experimental studies were interpreted as suggestive of the existence of a third metastable O_4 species in addition to the theoretically predicted molecules, namely, a relatively long lived complex between a ground-state O_2 molecule and an O_2 molecule in the excited $c^1\Sigma_u^-$ electronic state.[10]

To obtain conclusive proof, we have carried out an experiment aimed at detecting intact O_4. Our approach is also based, like previous studies,[8] on the neutralization of O_4^+ cations in the gas phase, but uses for the identification of the intact O_4 molecule neutralization reionization (NR) mass spectrometry[11] on a highly sensitive instrument that allowed the detection of other elusive atmospheric species, such as hydrogen trioxide[12] and the $[H_2O^+ \cdot O_2^-]$ charge-transfer complex.[13]

The O_4^+ ions were generated in a chemical ionization (CI) source by association of O_2 molecules with O_2^+ primary ions, formed both in the $X^2\Pi_g$ ground state and in electronically excited states by electron impact.[14] The ions were then accelerated through 4–8 keV, magnetically mass resolved, and probed by collisionally activated dissociation (CAD) mass spectrometry. Whereas the CAD spectrum of $^{16}O_4^+$ from the ionization of $^{16}O_2$ shows $^{16}O_2^+$ as the charged fragment, $^{16}O_2{}^{18}O_2^+$ ions from $^{16}O_2/^{18}O_2$ mixtures give $^{16}O_2^+$ and $^{18}O_2^+$ without the $^{16}O^{18}O^+$ ions[15] that would suggest isotopic scrambling (Figure 1). This shows that the O_4^+ ions probed contain two discrete O_2 units, each of which retains its original identity.

In the NR experiments the O_4^+ ions were also accelerated to 4–8 keV and mass-selected before undergoing two consecutive collision events in separate cells aligned along the beam path. In the first cell a fraction of the ions undergoes electron transfer from a target gas to yield O_4 together with neutral and charged fragments. All O_4^+ parent cations that escaped neutralization and any charged fragments were removed by a deflecting electrode, so that a beam containing only fast neutral species entered the second cell, where reionization by collision with a suitable target gas gives cations that are energy-selected, and their mass spectra are recorded. Detection of a "recovery" peak, that is, of a charged species with the same m/z ratio as the original O_4^+ ions demonstrates the occurrence of the sequence of Equation (1) and hence the existence of a neutral O_4 species with a lifetime that exceeds the flight time from the neutralization to the reionization cell.

$$O_4^+ \xrightarrow[\text{Neutralization}]{+M,\ -M^+} O_4 \xrightarrow[\text{Reionization}]{-e} O_4^+ \qquad (1)$$

The NR spectra of the $^{16}O_4^+$, $^{16}O_2{}^{18}O_2^+$, and $^{18}O_4^+$ ions, illustrated in Figure 2, show significant recovery peaks at $m/z = 64$, 68, and 72, respectively, a result that positively

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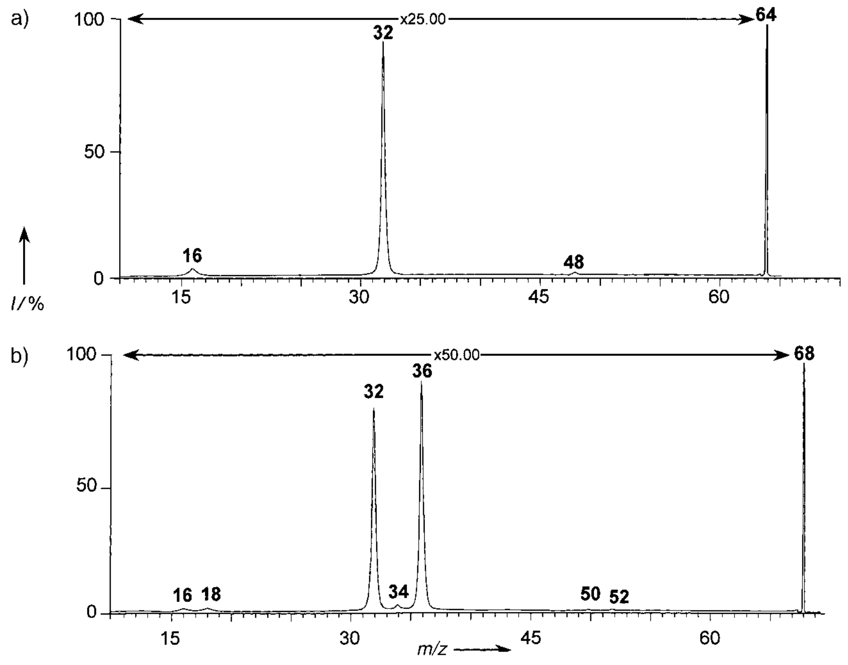

Figure 1. a) CAD spectrum of 8-kV $^{16}O_4^+$ ions, $m/z = 64$. Collision gas, He. b) CAD spectrum of $^{16}O_2{}^{18}O_2^+$ ions, $m/z = 68$.

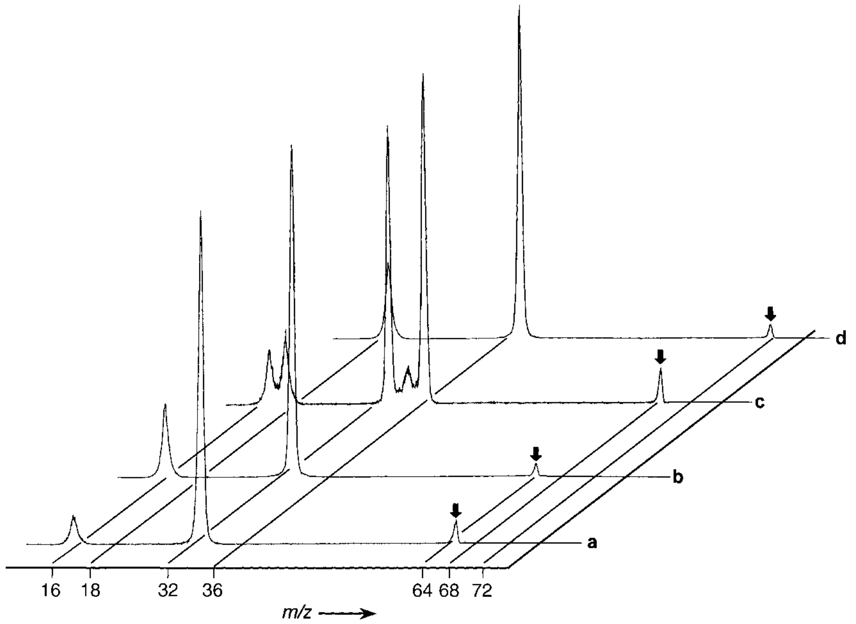

Figure 2. NR spectra of a) 4-kV $^{16}O_4^+$ ions, b) 6-kV $^{16}O_4^+$ ions, c) 6-kV $^{16}O_2{}^{18}O_2^+$ ions, and d) 6-kV $^{18}O_4^+$ ions. Note the recovery peaks at the appropriate m/z ratios in all spectra. Neutralizing gas, CH_4; reionizing gas, O_2 (see text).

establishes the existence of a neutral tetraoxygen species with a relatively long lifetime, whose lower limit of 0.95 ± 0.15 μs is defined by the flight time of an $^{18}O_4$ molecule with a mass of 72 Da and a kinetic energy of 4 keV from the neutralization to the reionization cell of the NR spectrometer.

Structural insight is provided by the isotopic composition of the charged fragments revealed by the NR spectra, which can originate only from the neutral species formed in one of the following processes: 1) The collision undergone by O_4^+ in the neutralization cell; 2) the unimolecular fragmentation of O_4 during its flight time; and 3) the collision undergone by O_4 in the reionization cell. As expected, $^{16}O_4$ gives $^{16}O_2^+$, $^{18}O_4$ gives $^{18}O_2^+$, and $^{16}O_2{}^{18}O_2$ gives nearly equal amounts of $^{16}O_2^+$ and $^{18}O_2^+$ without isotopically mixed $^{16}O^{18}O^+$ fragments[15] (Figure 2). This pattern strongly suggests, although it does not rigorously prove, that the neutral O_4 species detected contain two distinct O_2 units that become separated in the dissociation process(es) without exchanging their constituent atoms.

Having conclusively established the existence of long-lived metastable O_4, it is legitimate to inquire whether it can be identified as one of the species so far suggested. The following criteria can be applied: in general, NR mass spectrometry allows detection of a neutral species only if its dissociation requires overcoming a sizable barrier, on the order of 10 kcal mol^{-1}. Furthermore, the vertical character of the neutralization process allows survival of the neutral molecule only if its geometry is not significantly different from that of its charged parent (adequate Franck–Condon overlap).[11] Application of the above criteria to the O_4^+/O_4 system is particularly difficult, in view of the symmetry-breaking problem that affects the description of O_4^+, even by the most robust theoretical methods.[16] The structure of O_4^+ has been extensively investigated by IR and ESR spectroscopy in cryogenic Ne matrices[17] and by theoretical methods.[18] A comprehensive theoretical study indicates that a rectangular D_{2h} species and a *trans*-planar C_{2h} species are the most stable isomers, located 11.0 and 11.5 kcal mol^{-1}, respectively, below separated O_2^+ and O_2.[19] Symmetry-breaking problems were tackled by the complete active space state interaction (CASSI) method, which led to reassignment of the experimentally measured frequency of 1320 cm^{-1} to antisymmetric stretching of rectangular O_4^+.[20] A recent study of the performance of various theoretical methods weakened this assignment and additionally pointed to the failure of otherwise reliable methods such as BLYP and BPW91, which predict no bound solution at all for O_4^+, and further showed that the bond lengths calculated with a variety of methods by using both 6-31*G and cc-pVTZ basis sets show unusually wide variations.[16] If one considers that similar problems may conceivably affect the theoretical description of neutral O_4 as well, structural assignment of the experimentally observed O_4 species on theoretical grounds is clearly difficult. In principle, the relatively long lived species detected by NRMS could be a covalently bound molecule or some strongly bonded complex between two O_2 units. As to the first possibility, it appears that among the covalently bound O_4 molecules so far theoretically characterized, neither the D_{2d} quasisquare species nor the D_{3h} pinwheel species have a geometry sufficiently close to any of those assigned to the O_4^+ precursors detectable by NR mass spectrometry, in view of the unfavorable Franck–Condon factors involved. Furthermore, the calculated barrier for dissociation of the D_{2d} tetraoxygen molecule of 5.6 kcal mol^{-1},[4e] is somewhat lower than the threshold generally regarded as necessary to survive the vertical neutralization process. Finally, the fragmentation pattern in the NR spectrum is hardly consistent with those expected for either of the covalent molecules. Assuming a quasisquare D_{2d} structure in which all O–O bonds are equivalent, one would expect $^{16}O_2{}^{18}O_2$ to give, in addition to $^{16}O_2$ and $^{18}O_2$, a comparable $^{16}O^{18}O$ fragment, which is not displayed by the NR spectra.[15] As for the pinwheel D_{3h} molecule, its dissociation is expected to give, in addition to O and O_2, an O_3 fragment, also undetected in the NR spectrum.

Based on the above considerations, neither of the covalent molecules so far theoretically predicted is a particularly attractive candidate. Passing to O_4 complexes, that between a ground state O_2 molecule and one in the excited $c^1\Sigma_u^-$ state appears more compatible with the present results. As previously noted, its role has been stressed by Suits et al.,[10] based on their photoionization study of O_2 excited by DC discharges, and supported by ab initio calculations[9] and by Helm and Walter in a previous study of the neutralization of O_4^+ by Cs.[8] Consistent with their interpretation,[8, 10] neutralization of the $[c(^1\Sigma_u^-)O_2 \cdots O_2(X^3\Sigma_g^-)]$ complex populates a Rydberg state built on a core of O_2^+ in a $[O_2\ d^1\Pi_g(R) \cdots O_2(X^3\Sigma_g^-)]$ complex, that couples efficiently to the $[O_2(1^1\Pi_g) \cdots O_2(X^3\Sigma_g^-)]$ complex, which eventually decays by a fully allowed transition to the metastable $[O_2(c^1\Sigma_u^-) \cdots O_2(X^3\Sigma_g^-)]$ complex. This sequence accords well with the experimental finding that a fraction of the O_4^+ ions survives dissociation in the vertical neutralization process, since the weakly bound Rydberg electron is not expected to appreciably affect the geometry or the relatively large binding energy (ca. 10 kcal mol^{-1})[21] of the parent complex.[10] We further note that intervention of Rydberg states and formation of metastable O_4 species other than covalently bound molecules (e.g. ion-pair structures) have been suggested by Helm and Walter to account for the kinetic energy distribution of O_2 fragments from the neutralization of O_4^+ by Cs,[8] and that the lifetime of up to a few hundred nanoseconds of the metastable O_4 species inferred from their data is consistent with that measured in this work.

In conclusion, whereas a definitive assignment is not allowed by the present results, we are inclined to tentatively identify the O_4 species now positively detected as a long-lived complex between an O_2 molecule in the electronically excited $c^1\Sigma_u^-$ state and a ground state O_2 molecule, whereas the theoretically calculated features of the covalently bound O_4 molecules so far predicted appear less consistent with the experimental picture, although other structures cannot be rigorously excluded. Clearly, additional theoretical work is required to fully characterize metastable O_4, and hopefully the conclusive proof of its existence provided by this study will stimulate further calculations in this direction.

As a final note, the unabated interest in O_4 and its relevance to research areas other than atmospheric science are witnessed by recent studies on the red phase of solid oxygen at pressures of up to 63 GPa, whose IR spectrum is interpreted on the basis of a crystal composed by units formed by four atoms.[22, 23]

Experimental Section

The experiments were performed with a multisector mass spectrometer of the EBE-TOF configuration (ZABSpec oa-TOF, VG Micromass Ltd, Manchester), modified by addition of two pairs of collision gas cells and a CI source equipped with a thoriated filament. Typical source conditions were as follows: source temperature 100 °C; repeller voltage 0.0 V; ion-extraction voltage 4–8 kV; source pressure 0.05–0.1 Torr. The CAD and NR experiments were performed in the first of the collision cell pairs, located between the magnet and the second electrostatic analyzer. CAD spectra were recorded by utilizing He as the target gas, admitted into the first cell to a pressure adjusted to achieve a 80 % transmittance. In the NR experiments CH_4, utilized as the neutralizing gas, was also admitted into the first cell to achieve a beam transmission of 80 %. All charged species were then removed by a high-voltage (1 kV) deflector, and the fast neutral species entered the second cell, where reionization was achieved with O_2 as the stationary target gas. The NR spectra were averaged over 50 acquisitions to achieve a satisfactory signal-to-noise ratio. The gases were research-grade commercial products with a stated purity exceeding 99.99 mol %. The highly enriched $^{18}O_2$ sample (99 atom % ^{18}O) utilized in the NR experiments was obtained from IKON Stable Isotopes Inc.

In all NR experiments, and particularly in those where quite unusual species such as long-lived O_4 are observed, it is imperative to guard against conceivable interferences that are isobaric with the ionic parent(s) that are neutralized. In the case of interest, intervention of contaminants containing H, or other odd-mass atoms, can be safely excluded, based on the absence of detectable odd-mass fragments in the CAD and NR spectra of the $^{16}O_4^+$, $^{16}O_2{}^{18}O_2^+$, and $^{18}O_4^+$ ions utilized as the charged precursors. This leaves only impurities containing even-mass atoms such as S_2^+, SO_2^+, etc. These, and other conceivable, but much more unlikely candidates, were safely ruled out by the results of experiments involving O_4^+ ions labeled with ^{18}O; for example, no plausible impurity isobaric with $^{18}O_4^+$ ($m/z = 72$) exists.

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Fundamental Zeolite Crystal Growth Rates from Simulation of Atomic Force Micrographs**

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Insight into zeolite crystal growth is afforded by a computer model that simulates atomic force microscopy (AFM) images[1] of zeolite A crystallite surfaces. This leads to the first ever quantification of fundamental zeolite crystal growth processes. AFM enables imaging of nonconducting surfaces with atomic-scale vertical resolution and is ideal for probing the surface of inorganic crystals. The first AFM image of a zeolite, which depicted the cleaved (100) face of clinoptilolite, was published by Weisenhorn et al. in 1990.[2] This triggered a series of mineral zeolite studies[3] that used extremely detailed topographical information obtained from AFM images to estimate unit cell parameters. At lower resolution the imaging of atomic corrugations is precluded; however, there still remains a great wealth of information to be garnered concerning crystal growth processes.

Zeolite growth often occurs by the deposition of successive layers thus creating surface terraces.[1] Typically, terrace height, orientation, and shape are governed by the unit-cell structure and symmetry of the zeolite. Terrace separation usually decreases towards the extremity of the growing face, thus generating an overall parabolic cross-section. This quadratic relationship implies that it is terrace area and not size that grows at constant rate.[1b] Constant-area-deposition growth therefore predominates and this has significant ramifications on the mode of transport of gel nutrient to the growing face, as will be discussed later. As an introduction, an overview is given of specific features observed on the surface of zeolite A, chosen owing to its paramount industrial importance, cubic symmetry (facilitating creation of the model), and the existence of high-quality AFM images of its surface.

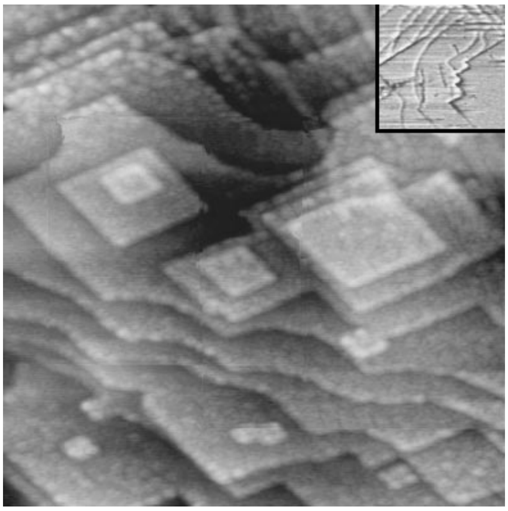

Figure 1. 1.0 × 1.0 μm^2 AFM Tapping Mode image of a portion of a 10.0 × 10.0 μm^2 (100) face of a zeolite A crystallite. Inset: phase image showing a section with a convex terrace growth front.

Atomic force micrographs of the (100) face of zeolite A crystallites reveal square-shaped surface terraces of uniform height equal to 1.2 nm, that is half the unit-cell dimension (Figure 1; squares are distorted to parallelograms owing to crystal tilt). The terrace edges run parallel to the edges of the crystal face. A further feature is that of curved terrace edges that have been postulated to arise during the coalescence of individual nucleation centers.[1b] The shape and surface density of these terraces are a result of the crystal growth mechanism. This work is concerned with simulation of such AFM images using the rates of fundamental crystal growth processes as variables in the model.

These AFM observations serve both as a basis for creation of the computer code and also provide a means of testing the

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