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**ERNEST ORLANDO LAWRENCE  
BERKELEY NATIONAL LABORATORY**

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**Nuclear Science Division**

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## **Unraveling the Mysteries of Metastable O<sub>4</sub>**

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January 1999

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# Unraveling the mysteries of metastable $O_4^*$

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## Abstract

A recent report from our laboratory described 1+1 resonant photoionization spectra of an energetic, metastable  $O_4$  species produced in a DC discharge [H. Bevsek et al., *Farad. Discuss.* **108** 131 (1998)]. These intense spectra were observed as many lines throughout the region from 280 to 325 nm, implying an initial form of tetraoxygen containing 4 eV internal energy relative to  $O_2 + O_2$ . Although a definitive assignment of the spectra was lacking, the long-predicted covalent forms of  $O_4$ , either cyclic ( $D_{2d}$ ) or 'pinwheel' ( $D_{3h}$ ), were adduced as possible candidates. We here present rotationally resolved photoionization spectra, photoelectron spectra, and *ab initio* calculations providing strong evidence for the identity of this species as a novel complex between a ground state  $O_2$  molecule and one in the  $c(1^1\Sigma_u^-)$  state, which is excited via an allowed transition to the  $1(1^1\Pi_g)$  valence state. The latter then couples to the  $d(1^1\Pi)$  Rydberg state, shifted in energy owing to the presence of the adjacent  $O_2$  molecule, from which it then ionizes. The results underscore the potential importance of the fully allowed but overlooked  $1(1^1\Pi_g) \leftarrow c(1^1\Sigma_u^-)$  electronic transition in  $O_2$  in the near ultraviolet, and provide a simple interpretation of puzzling results in an earlier study of electron transfer to  $O_4^+$  [H. Helm and C. W. Walter, *J. Chem. Phys.* **98** 5444 (1993)].

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order of 3.2-3.6 cm<sup>-1</sup>. Similar rotational structure is also apparent on some lines in the 306 nm region, although not as pronounced.

Photoelectron spectra have been recorded using the VELMI technique [13] on many of these resonant lines. Typical images and the corresponding electron kinetic energy release distributions are shown in Fig. 2 for several resonant lines. Most of the observed lines show electron kinetic energy distributions dominated by single electron energy peaks. For the long wavelength region, these are all very near threshold (less than 50 meV). In the region around 306 nm, again mostly single sharp peaks are observed, below 50 meV or so. However, occasionally some multiple peaks and some broader peaks are seen in this region. Two kinds of behavior are seen on the lines occurring between 290-298 nm: either single peaks at about 0.5 eV, or double peaks around this energy with a spacing of 190 meV (1550 cm<sup>-1</sup>).

If one of the covalent species is responsible for these spectra, then two critical issues are: 1) accounting for the observed ionization potential of  $\sim 8$  eV from the metastable state or likely 12 eV or so from two ground state O<sub>2</sub> molecules, and 2) finding a bound excited state  $\sim 4$  eV above the metastable species. To this end, we have performed accurate coupled-cluster (CC) calculations with the ACES II program system [14]. We use a TZ2P basis of Cartesian Gaussians contracted as (11s6p3d)/[5s3p2d] [15] except as indicated. Table 1 presents computed CCSD and CCSD(T) [16,17] energies relative to two ground state O<sub>2</sub> molecules for several states of interest. At the CCSD(T) level, we find two covalent forms, the cyclic (D<sub>2d</sub>) at 5.30 eV and the pinwheel (D<sub>3h</sub>) at 6.52 eV. The detailed structure and vibrational frequencies of the two species are in Table 2, among those for other interesting states. Shown in Table 3 are the IP-EOM-CCSD [16,17] vertical ionization potentials for the two covalent forms. The lowest IP's occur at 10.98 for the cyclic and 12.47 for the pinwheel structures. However, this is much higher than the energy of two photons at 300 nm ( $\sim 8$  eV), thus outside the range of the experiment. The adiabatic IP's for the two forms are in Table 1 and their structures in Table 2. To the contrary, only the two nearly degenerate <sup>4</sup>B<sub>u</sub> C<sub>2h</sub> and <sup>4</sup>B<sub>1g</sub> D<sub>2h</sub> ionized van der Waals complexes are close to the 12 eV energy. Our result of 11.95 eV is in excellent agreement with the 11.67 eV CASSCF value of Lindh and Barnes [18].

The other question pertains to the existence of a bound excited state of the covalent species that is 8 eV above the two O<sub>2</sub>'s and whose vibrational frequencies have been previously estimated [11]. STEOM-CC [19] calculations in the POL1 basis [15] at the geometry of the D<sub>2d</sub> ground state shows a weakly allowed E state at 7.10 eV and a dipole forbidden A<sub>2</sub> state at 8.54 eV and three others weakly allowed, between 9.0 and 9.4 eV. For the D<sub>3h</sub> form, the first state is a forbidden A<sub>1</sub> which occurs at 7.23 eV with a strong E' state at 8.92 eV, with the next (dipole forbidden) A<sub>2</sub> state at 11.0 eV. There are five triplet states in the range of 8 to 9 eV for the D<sub>2d</sub> form, with the lowest (an E state) at 6.26. The triplet states start at 7.05 eV for the D<sub>3h</sub> isomer, with an E'' state at 8.72. However, despite extensive effort, when optimizing the geometry for excited states either with CCSD when applicable, or EOM-CCSD analytical gradient techniques [20] otherwise to determine if there were bound excited states, only two were found, one singlet and one triplet. Their zero point corrected adiabatic excitation energies, structures and frequencies are shown in Tables 1 and 2. Neither the energies nor the frequencies make a persuasive case for this being the possible intermediate state in the 1+1 experiment.

From the experimental standpoint, one significant aspect of the observations argues in

diagonal Franck-Condon factors between the Rydberg and the ion. If this picture is accurate for O<sub>4</sub>, it is perhaps surprising that no O<sub>2</sub><sup>+</sup> is seen; this implies some significant differences for the ionization dynamics in the complex as opposed to the free O<sub>2</sub> molecule. In fact, it is precisely in the nature of these Rydberg-valence interactions that we can expect a profound impact of the formation of the van der Waals complex. This is because the Rydberg state will be greatly stabilized in the complex-nearly to the extent of the 0.45 eV bond in O<sub>2</sub>-O<sub>2</sub><sup>+</sup>. The valence state curves will be little-perturbed in comparison. The location of the Rydberg and ion curves for the complex are shown as dashed lines in Fig. 3. This shift must have dramatic effects on the Rydberg-valence coupling as well; further study will be needed to unravel this aspect of the problem. In any case this provides a reasonable explanation for the absence of the O<sub>2</sub><sup>+</sup> in these experiments despite the likelihood that the number density of free O<sub>2</sub> c(<sup>1</sup>Σ<sub>u</sub><sup>-</sup>) molecules is much greater than those involved in complexes. It is likely that the fate of the free O<sub>2</sub>, upon excitation to the 1(<sup>1</sup>Π<sub>g</sub>) state, is either predissociation via the 2<sup>1</sup>Π<sub>g</sub> state, or by the triplet states interacting with the d state.

Many of the experimental results can be satisfactorily accounted for by invoking this complex. The rotational spacing in the long wavelength region, about 3.5 cm<sup>-1</sup>, is very near 4B<sub>e</sub> for the c(<sup>1</sup>Σ<sub>u</sub><sup>-</sup>) state (B<sub>e</sub> = 0.9 cm<sup>-1</sup>). This would be expected, for example, for a T-shaped complex wherein one of the rotational constants will resemble that of one of the O<sub>2</sub> molecules. The photoelectron spectra, dominated by single peaks, arise owing to the fact that the ionization takes place from a complex involving the d(<sup>1</sup>Π<sub>g</sub>) Rydberg state so that Δv = 0 transitions dominate as mentioned above. Finally, the absence of O<sub>2</sub><sup>+</sup> is readily explained by the very different Rydberg-valence interactions in the complex as opposed to the free O<sub>2</sub>. This picture also accounts for some unusual spectra reported in a closely related study by Helm and Walter [24]. Their experiments were similar to the studies of van der Zande et al, but used charge transfer to O<sub>4</sub><sup>+</sup> rather than O<sub>2</sub><sup>+</sup>. They reported clearly resolved vibrational structure in the O<sub>2</sub> product kinetic energy distributions following charge transfer from cesium, which they reluctantly ascribed to coincident formation of two O<sub>2</sub> molecules in v=29, a rather unlikely process. This was necessary to account for the vibrational spacing of 800 cm<sup>-1</sup> observed in the O<sub>2</sub> kinetic energy release distributions. Our alternative interpretation of their results suggests simply the reverse of the ionization process outlined above: electron transfer from cesium populates the Rydberg state around 7.6 eV, which then couples efficiently to the metastable O<sub>2</sub> X(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>)-O<sub>2</sub> 1(<sup>1</sup>Π<sub>g</sub>) complex. We suggest the structure in the kinetic energy release distributions of Helm and Walter simply reflects the vibrational structure in the metastable state. For the Herzberg states, the vibrational frequencies are all on the order of 800 cm<sup>-1</sup>; the vibrational frequency in the 1(<sup>1</sup>Π<sub>g</sub>) state is likely to be similar.

It is worthy to note that although these spectra are not associated with covalently bound, energetic O<sub>4</sub> species, this does not imply that the latter are not formed; indeed they may well be present in the molecular beam. Different techniques will be required to probe for those species. Future experiments will also allow direct probing of this 1(<sup>1</sup>Π<sub>g</sub>) ← c(<sup>1</sup>Σ<sub>u</sub><sup>-</sup>) transition in O<sub>2</sub>, using photofragment excitation spectroscopy and two color UV + VUV spectroscopy. These studies are underway.

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Table 2. Computed structures, harmonic frequencies and intensities for the relevant forms of O<sub>4</sub> in Table 1. Bond distances are in Angstroms, frequencies are in cm<sup>-1</sup>, and intensities for dipole-allowed modes are shown at the highest level of theory in units of km mol<sup>-1</sup>.

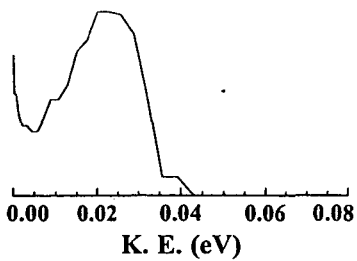
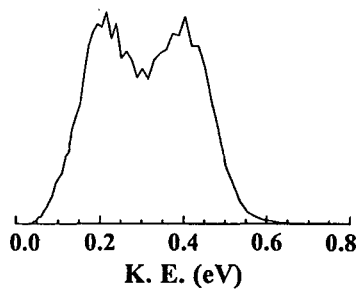
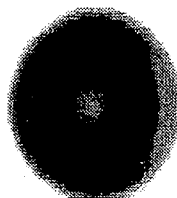
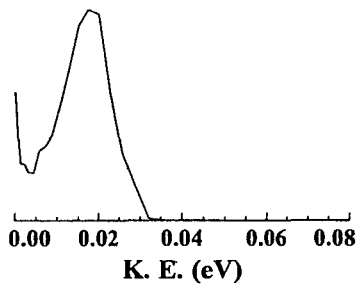
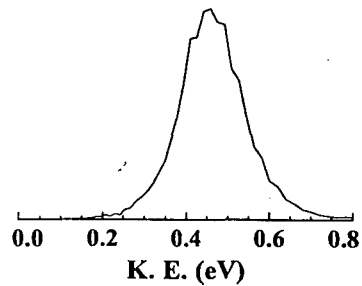
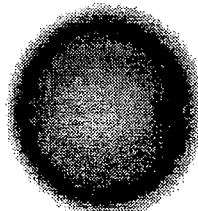
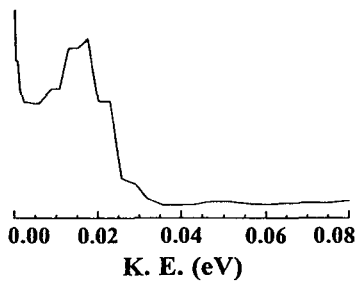
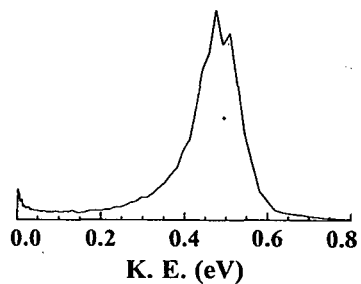
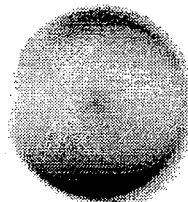
		HF	MBPT(2)	CCSD	CCSD(T)
<sup>1</sup> A <sub>1</sub> D <sub>2d</sub>	R	1.392	1.483	1.460	1.486
	dihedral	20.4	28.8	26.6	27.9
	A <sub>1</sub>	353	411	402	400
	E	1107	703	816	702 (0.00)
	frequencies(intensities) B <sub>2</sub>	1062	779	856	798 (0.11)
	B <sub>1</sub>	1245	851	930	809
	A <sub>1</sub>	1222	895	985	897
<sup>2</sup> B <sub>2u</sub> D <sub>4h</sub> ionized state	R	1.326	1.454	1.397	1.423
	B <sub>2u</sub>	405	494	329	292
	B <sub>1g</sub>	1250	798	975	898
	A <sub>1g</sub>	1359	789	1064	961
	B <sub>2g</sub>	1468	958	1184	1086
	E <sub>u</sub>	999i	2257	1342	852 (0.10)
<sup>1</sup> A <sub>1</sub> ' D <sub>3h</sub>	R	1.240	1.304	1.290	1.312
	E'	596	631	585	559 (5.42)
	A <sub>2</sub> '	779	666	666	609 (1.69)
	E'	1026	1861	1030	988 (186.17)
	A <sub>1</sub> '	1035	928	902	828
<sup>1</sup> A <sub>2</sub> C <sub>3v</sub> excited state	R		1.324	1.330	
	angle		116.3	115.7	
	E		188	126 (4.56)	
	A <sub>1</sub>		492	485 (4.63)	
	E		1252	717 (9.59)	
	A <sub>1</sub>		936	867 (0.30)	
<sup>3</sup> A <sub>2</sub> C <sub>3v</sub> excited state	R	1.323	1.363	1.357	1.396
	angle	113.2	111.4	112.7	112.8
	E	435	382	288	
	A <sub>1</sub>	507	626	426	
	A <sub>1</sub>	924	1117	828	
	E	1220	2367	932	
<sup>4</sup> A <sub>2</sub> C <sub>3v</sub> ionized state	R	1.360	1.389	1.400	1.415
	angle	113.6	112.2	111.3	111.0
	E	488	449	409	
	A <sub>1</sub>	414	443	438	
	A <sub>1</sub>	858	912	788	
	E	1022	977	760	

## FIGURES

FIG. 1. Raw  $O_4^+$  photoion yield and total photoelectron yield spectra. Expanded region of electron spectrum is shown in inset.

FIG. 2. Photoelectron images and electron kinetic energy release distributions for several resonant lines of  $O_4^*$ . Wavelengths are: A) 323.478 nm, B) 306.122 nm, C) 304.987 nm D) 296.788 nm, E) 294.893 nm and F) 282.836 nm.

FIG. 3. Relevant potential curves adapted from Ref. [23], from calculations of Ref. [21]. The Rydberg and ion curves, duplicated and offset -0.45 eV (the energy of the  $O_2-O_2^+$  bond) are shown as dashed lines (see text).

**A****D****B****E****C****F**

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