

LBNL-42642
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Remnants of Initial Anisotropic High Energy Density Domains in Nucleus-Nucleus Collisions

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December 1998

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Physical Review C



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Unraveling the Mysteries of Metastable O₄

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January 1999

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and U.S. Air Force Office of Scientific Research Grant No. F-49620-95-1-0130.

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Abstract

A recent report from our laboratory described 1+1 resonant photoionization spectra of an energetic, metastable O₄ 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 O₂ + O₂. Although a definitive assignment of the spectra was lacking, the long-predicted covalent forms of O₄, 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 O₂ molecule and one in the c(¹Σ_u⁻) state, which is excited via an allowed transition to the 1(¹Π_g) valence state. The latter then couples to the d(¹Π) Rydberg state, shifted in energy owing to the presence of the adjacent O₂ molecule, from which it then ionizes. The results underscore the potential importance of the fully allowed but overlooked 1(¹Π_g) ← c(¹Σ_u⁻) electronic transition in O₂ in the near ultraviolet, and provide a simple interpretation of puzzling results in an earlier study of electron transfer to O₄⁺ [H. Helm and C. W. Walter, *J. Chem. Phys.* **98** 5444 (1993)].

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order of $3.2\text{-}3.6\text{ cm}^{-1}$. 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^{-1}).

If one of the covalent species is responsible for these spectra, then two critical issues are: 1) accounting for the observed ionization potential of ~ 8 eV from the metastable state or likely 12 eV or so from two ground state O_2 molecules, and 2) finding a bound excited state ~ 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_2 molecules for several states of interest. At the CCSD(T) level, we find two covalent forms, the cyclic (D_{2d}) at 5.30 eV and the pinwheel (D_{3h}) 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 (~ 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 4B_u C_{2h} and ${}^4B_{1g}$ D_{2h} 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_2 '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_{2d} ground state shows a weakly allowed E state at 7.10 eV and a dipole forbidden A_2 state at 8.54 eV and three others weakly allowed, between 9.0 and 9.4 eV. For the D_{3h} form, the first state is a forbidden A_1 which occurs at 7.23 eV with a strong E' state at 8.92 eV, with the next (dipole forbidden) A_2 state at 11.0 eV. There are five triplet states in the range of 8 to 9 eV for the D_{2d} form, with the lowest (an E state) at 6.26. The triplet states start at 7.05 eV for the D_{3h} 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 O₄, it is perhaps surprising that no O₂⁺ is seen; this implies some significant differences for the ionization dynamics in the complex as opposed to the free O₂ 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 O₂–O₂⁺. 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 O₂⁺ in these experiments despite the likelihood that the number density of free O₂ c(¹Σ_u⁻) molecules is much greater than those involved in complexes. It is likely that the fate of the free O₂, upon excitation to the 1(¹Π_g) state, is either predissociation via the 2¹Π_g 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⁻¹, is very near 4B_e for the c(¹Σ_u⁻) state (B_e = 0.9 cm⁻¹). This would be expected, for example, for a T-shaped complex wherein one of the rotational constants will resemble that of one of the O₂ molecules. The photoelectron spectra, dominated by single peaks, arise owing to the fact that the ionization takes place from a complex involving the d(¹Π_g) Rydberg state so that Δv = 0 transitions dominate as mentioned above. Finally, the absence of O₂⁺ is readily explained by the very different Rydberg-valence interactions in the complex as opposed to the free O₂. 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 O₄⁺ rather than O₂⁺. They reported clearly resolved vibrational structure in the O₂ product kinetic energy distributions following charge transfer from cesium, which they reluctantly ascribed to coincident formation of two O₂ molecules in v=29, a rather unlikely process. This was necessary to account for the vibrational spacing of 800 cm⁻¹ observed in the O₂ 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 O₂ X(³Σ_g⁻)–O₂ 1(¹Π_g) 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⁻¹; the vibrational frequency in the 1(¹Π_g) state is likely to be similar.

It is worthy to note that although these spectra are not associated with covalently bound, energetic O₄ 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(¹Π_g) ← c(¹Σ_u⁻) transition in O₂, using photofragment excitation spectroscopy and two color UV + VUV spectroscopy. These studies are underway.

Acknowledgments. AGS acknowledges helpful conversations concerning O₄ with many

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Table 2. Computed structures, harmonic frequencies and intensities for the relevant forms of O_4 in Table 1. Bond distances are in Angstroms, frequencies are in cm^{-1} , and intensities for dipole-allowed modes are shown at the highest level of theory in units of km mol^{-1} .

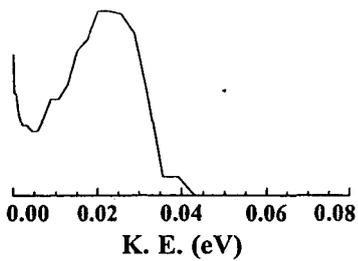
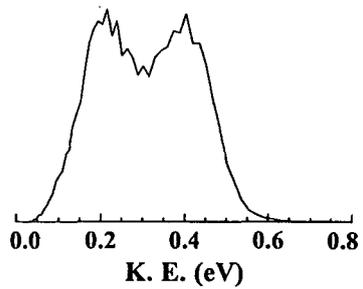
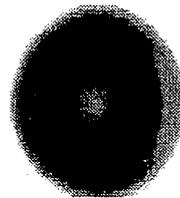
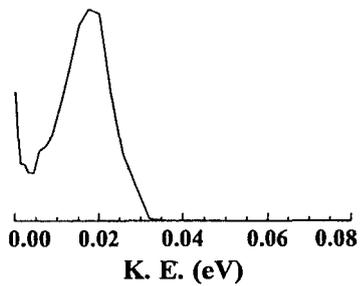
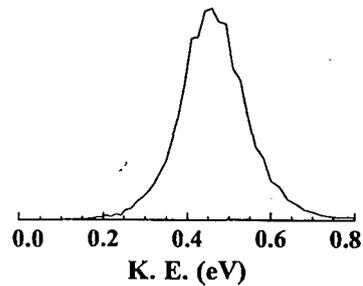
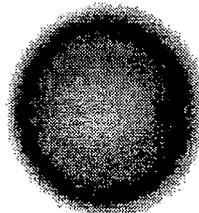
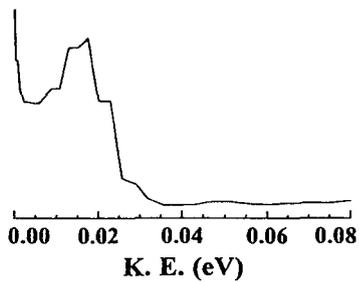
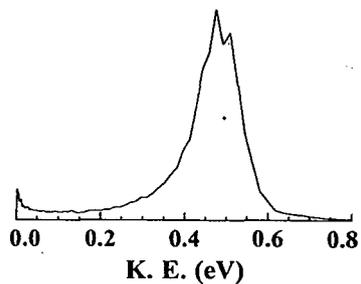
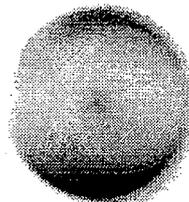
		HF	MBPT(2)	CCSD	CCSD(T)
$^1A_1 D_{2d}$	R	1.392	1.483	1.460	1.486
	dihedral	20.4	28.8	26.6	27.9
	frequencies(intensities)				
	A_1	353	411	402	400
	E	1107	703	816	702 (0.00)
	B_2	1062	779	856	798 (0.11)
	B_1	1245	851	930	809
	A_1	1222	895	985	897
$^2B_{2u} D_{4h}$ ionized state	R	1.326	1.454	1.397	1.423
	B_{2u}	405	494	329	292
	B_{1g}	1250	798	975	898
	A_{1g}	1359	789	1064	961
	B_{2g}	1468	958	1184	1086
	E_u	999i	2257	1342	852 (0.10)
$^1A'_1 D_{3h}$	R	1.240	1.304	1.290	1.312
	E'	596	631	585	559 (5.42)
	A_2''	779	666	666	609 (1.69)
	E'	1026	1861	1030	988 (186.17)
	A_1'	1035	928	902	828
$^1A_2 C_{3v}$ excited state	R		1.324	1.330	
	angle		116.3	115.7	
	E		188	126 (4.56)	
	A_1		492	485 (4.63)	
	E		1252	717 (9.59)	
	A_1		936	867 (0.30)	
$^3A_2 C_{3v}$ 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_1	507	626	426	
	A_1	924	1117	828	
	E	1220	2367	932	
$^4A_2 C_{3v}$ 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_1	414	443	438	
	A_1	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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