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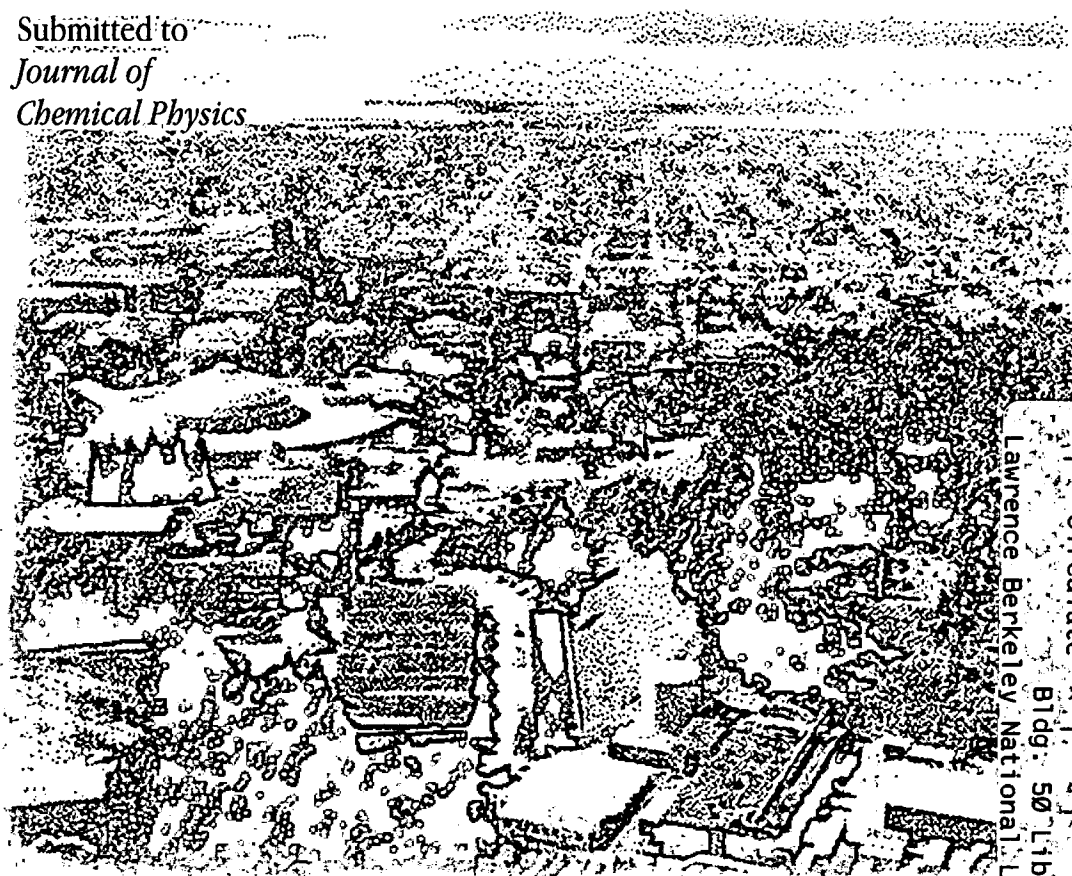
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Arthur G. Suits, Kenneth J. Wilson,
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and Rodney J. Bartlett

Chemical Sciences Division

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Unraveling the Mysteries of Metastable O₄

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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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Interest in tetraoxygen molecules dates to a 1924 paper by G. N. Lewis [1]; since then, studies of O₂ dimers have enjoyed a long history of investigation [2–4] both in an effort to understand the weak visible absorption that is responsible for the color of condensed O₂ and to explore their importance in the atmospheric radiation budget. Theoretical studies of covalently bound O₄ species began with Adamantides' 1980 prediction [5] of a bound cyclic (D_{2d}) form. This stimulated considerable further theoretical effort as this cyclic O₄, nearly 4 eV higher in energy than two O₂ molecules, appeared to be a promising candidate for a high energy density material [6–8]. Subsequent theoretical studies have also identified a D_{3h} form analogous to SO₃ at a somewhat higher energy [9,10]. Although experimentalists have long observed evidence of van der Waals' complexes of ground state O₂ molecules, no evidence has been found supporting the theoretical predictions of covalent O₄ species. In a recent report from our laboratory, 1+1 resonant photoionization spectra were reported for an energetic, metastable O₄ species produced in a DC discharge [11]. Intense spectra were observed throughout the region from 280 to 325 nm, implying an initial form of tetraoxygen containing at least 4 eV internal energy relative to O₂ + O₂, as well as the existence of a higher excited state through which the ionization takes place. In the absence of plausible alternatives accounting for all the observations, an energetic covalent O₄ species was considered the most likely candidate. In this Communication, we present rotationally resolved photoionization spectra, photoelectron spectra and *ab initio* calculations that provide compelling indirect evidence pointing to the identity of this species as a novel complex involving one ground state O₂ molecule and one in the metastable c(¹Σ_u⁻) state.

The experiment [11,12] consists in passing a pulsed molecular beam of oxygen through electrodes held at ground and ±3-5kV so that the discharge occurs in the collision region of the beam. The discharge is positively biased when detecting ions, and negatively biased when detecting electrons to inhibit interference from corresponding species in the beam. The molecular beam is skimmed before entering a main chamber wherein it is crossed by an unfocused (for wavelength scans) or loosely focused (for photoelectron spectra) Nd-YAG pumped dye laser doubled to yield light tunable around 300 nm with a linewidth on the order of 0.08 cm⁻¹. The laser and molecular beams cross on the axis of a time-of-flight mass spectrometer with velocity map imaging [13] (VELMI) detector, allowing for several different kinds of experiments to be performed. Mass-selected resonant ionization scans are effected by recording the total mass-selected ion yield as a function of laser wavelength. Total photoelectron signals are similarly obtained by reversing the potentials and recording the integrated electron signal striking the detector as a function of laser wavelength. Photoelectron images are recorded on the resonant lines using the VELMI technique, calibrated with Ar* ionization, and converted to electron kinetic energy using established techniques.

Photoionization spectra recorded for m/e=64, O₄⁺ are shown for the region from 302 to 325 nm in Fig. 1. Total photoelectron yield signals are also shown; these signals are recorded under conditions in which the discharge bias is reversed and the total discharge power in the electron case is lower (2.5 Watts vs. 6 Watts). We ascribe the differences in the ion and electron spectra to inherent noise in the higher power ion scans and the correspondingly higher temperature of the ion scans, giving more 'hot band' contributions. Under the conditions of the experiment, virtually no ions are observed other than O₄⁺. Inset in Fig. 1 is an expanded view of the electron yield spectrum in the long wavelength region near 323 nm. Clearly resolved rotational spectra are observed, with line spacings on the

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

favor of one of the covalent O_4 molecules: these neutral metastable O_4 species are formed in the harsh conditions of the discharge and survive at least 80 microseconds from the discharge to the probe region in which they are ionized; moreover, they are always observed as O_4^+ rather than O_2^+ . At first glance, this makes van der Waals species seem unlikely. However, convincing *ab initio* calculations predict energies for the ionized covalent forms beyond the reach of the experiment. Furthermore, the rotationally resolved spectra in the inset in Fig. 1 show line spacing that is very difficult to reconcile with one of the large covalently bound species where the low rotational constants shown are in Table 1. Even accounting for the nuclear spin symmetry for the D_{3h} species, a line spacing on the order of $6B_e$ or 1.2 cm^{-1} is expected. Taking all these points into consideration, covalently bound energetic tetraoxygen molecules do not appear likely to be responsible for the experimental observations.

We now consider electronically excited van der Waals complexes. There are several metastable states of O_2 that may form long-lived van der Waals complexes of the correct energy. The relevant potential energy curves for O_2 are shown in Fig. 3. Complexes involving lower lying metastable singlet states are known, but have neither sufficient energy nor plausible ionization paths to be responsible for the experimental observations. The Herzberg states of O_2 , however, do appear at the correct energy to form complexes that could give rise to the observed spectra. One of these, the $c(^1\Sigma_u^-)$ state, is shown in Fig. 3 based on calculations of Saxon and Liu [21], adapted from van der Zande et al. [22,23] This is the only species that appears to be of the correct symmetry to possess an allowed optical transition in this wavelength region. Furthermore, there exists an excited $1(^1\Pi_g)$ state very near the energy of our probe transition, i.e. about 4 eV above the c state. However, earlier calculations indicated that this $1(^1\Pi_g)$ state is repulsive, adiabatically correlating with two ground state oxygen atoms. In a very relevant series of experiments [22,23] looking at atomic fragments following charge transfer from cesium atoms to O_2^+ , van der Zande et al. explored the nonadiabatic dynamics and coupling among several of the curves in Fig. 3 (and with triplet curves not shown). Most importantly, they showed that the $1(^1\Pi_g)$ and $2(^1\Pi_g)$ curves indicated in Fig. 3 do not interact strongly, and may be viewed in a 'diabatic' picture, as shown; the $1(^1\Pi_g)$ level is then a bound or quasibound state. The $1(^1\Pi_g) \leftarrow c(^1\Sigma_u^-)$ transition of O_2 is thus a strongly allowed optical transition in O_2 with nearly diagonal Franck-Condon factors in the region of 280-330 nm. It is not clear that this important implication of the observations of van der Zande et al. has been recognized. However, direct ionization of this $1(^1\Pi_g)$ state is not possible in this wavelength region, since it yields the excited $a(^4\Pi)$ state of the ion an additional 8 eV above the $1(^1\Pi_g)$ -state. In fact, the experiments of van der Zande and coworkers show the importance of the interactions involving the $1(^1\Pi_g)$ valence state and the $d(^1\Pi_g)$ Rydberg state that was initially prepared in their experiments; a path to ionization is clearly present in this wavelength region via the valence-Rydberg interactions.

This provides a likely scenario for this 1+1 ionization process in O_4^* , indicated by the heavy arrows in Fig. 3. If we begin with a van der Waals complex between $O_2 X(^3\Sigma_u^-)$ and $O_2 c(^1\Sigma_u^-)$, a fully allowed electronic transition localized on the c state molecule takes us to a complex involving the $1(^1\Pi_g)$ state. This state can either predissociate to give oxygen atoms, or couple to the $d(^1\Pi_g)$ Rydberg state, or the system can dissociate to two O_2 molecules. It is likely that all of these occur, no doubt with a strong dependence upon the initially excited vibrational level. If the Rydberg complex is formed, it can then ionize easily in this wavelength region, and the ionization will be dominated by $\Delta v = 0$ transitions owing to the

diagonal Franck-Condon factors between the Rydberg and the ion. If this picture is accurate for O_4 , it is perhaps surprising that no O_2^+ is seen; this implies some significant differences for the ionization dynamics in the complex as opposed to the free O_2 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 $O_2-O_2^+$. 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_2^+ in these experiments despite the likelihood that the number density of free O_2 $c(1\Sigma_u^-)$ molecules is much greater than those involved in complexes. It is likely that the fate of the free O_2 , upon excitation to the $1(1\Pi_g)$ state, is either predissociation via the $2^1\Pi_g$ 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 $c(1\Sigma_u^-)$ state ($B_e = 0.9\text{ cm}^{-1}$). This would be expected, for example, for a T-shaped complex wherein one of the rotational constants will resemble that of one of the O_2 molecules. The photoelectron spectra, dominated by single peaks, arise owing to the fact that the ionization takes place from a complex involving the $d(1\Pi_g)$ Rydberg state so that $\Delta v = 0$ transitions dominate as mentioned above. Finally, the absence of O_2^+ is readily explained by the very different Rydberg-valence interactions in the complex as opposed to the free O_2 . 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_4^+ rather than O_2^+ . They reported clearly resolved vibrational structure in the O_2 product kinetic energy distributions following charge transfer from cesium, which they reluctantly ascribed to coincident formation of two O_2 molecules in $v=29$, a rather unlikely process. This was necessary to account for the vibrational spacing of 800 cm^{-1} observed in the O_2 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 $O_2 X(3\Sigma_g^-)-O_2 1(1\Pi_g)$ 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 $1(1\Pi_g)$ state is likely to be similar.

It is worthy to note that although these spectra are not associated with covalently bound, energetic O_4 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 $1(1\Pi_g) \leftarrow c(1\Sigma_u^-)$ transition in O_2 , using photofragment excitation spectroscopy and two color UV + VUV spectroscopy. These studies are underway.

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Table 1. Computed CCSD and CCSD(T) relative energies and rotational constants at optimal geometries for O₄ species. The relative energies, in units of eV's, are with respect to O₂ X(³Σ_g⁻) + O₂ X(³Σ_g⁻) and rotational constants are from CCSD(T) geometries in cm⁻¹.

		CCSD	CCSD(T)	rotational constants (B _e)		
	¹ A ₁ D _{2d}	4.36	5.30	0.254	0.478	0.478
	² B _{2u} D _{4h} ionized state	15.14	15.89	0.260	0.520	0.520
	¹ A ₁ ' D _{3h}	5.66	6.52	0.204	0.408	0.408
covalent	¹ A ₂ C _{3v} excited state ¹	6.46		0.208	0.406	0.406
	³ A ₂ C _{3v} excited state	6.69	6.36	0.195	0.374	0.374
	⁴ A ₂ C _{3v} ionized state	17.39	18.49	0.194	0.368	0.368
vdW	⁴ B _u C _{2h} ionized state	11.67	11.95	0.149	0.185	0.769
	⁴ B _{1g} D _{2h} ionized state	11.67	11.95	0.149	0.185	0.769

¹For this species, rotational constants are from the EE-EOM-CCSD geometry.

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
	A ₁	353	411	402	400
	E	1107	703	816	702 (0.00)
	frequencies(intensities) 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	

Table 3. Lowest vertical ionization potentials for the two covalently bound forms of O₄. The nuclear geometry for these calculations was the optimized CCSD(T)/TZ2P for the ground state.

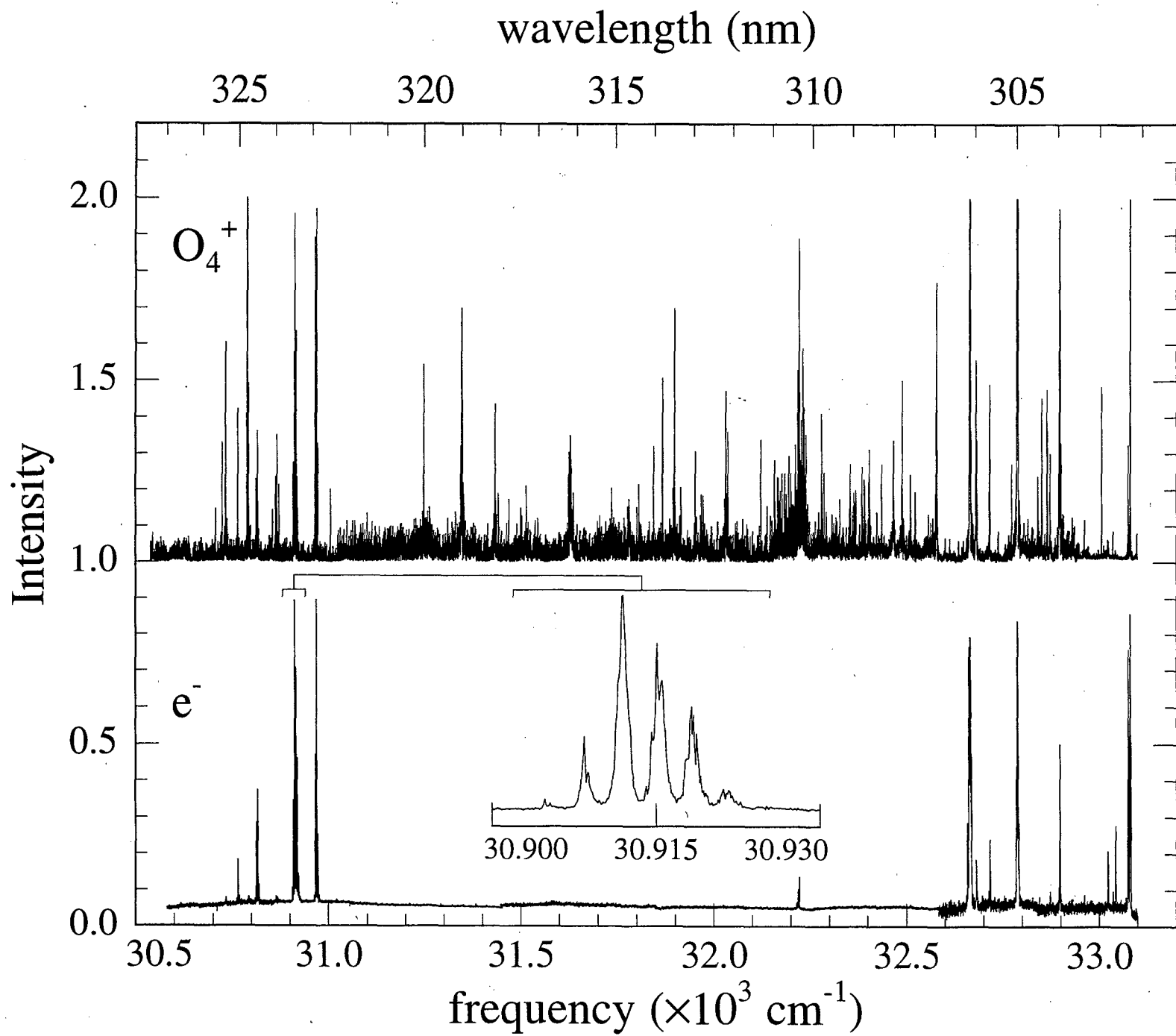
MO	Koopmans		IP-EOM-CCSD	
	TZ2P	POL1	TZ2P	POL1
4a ₁	13.58	13.67	10.98	10.87
D _{2d} 4e	15.69	15.80	13.18	13.09
3e	17.49	17.58	16.19	16.20
1a ₂ '	15.42	15.46	12.47	12.33
D _{3h} 1e''	14.43	14.47	13.04	12.96
4e'	16.53	16.58	14.02	13.93

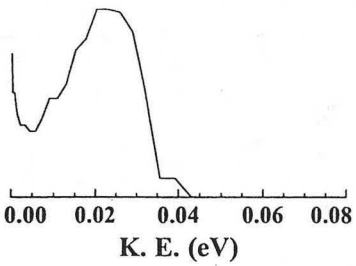
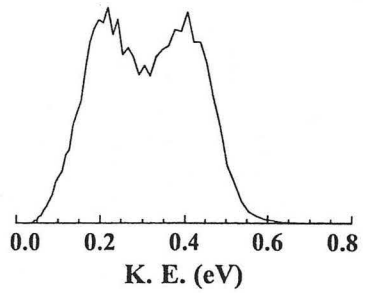
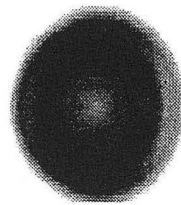
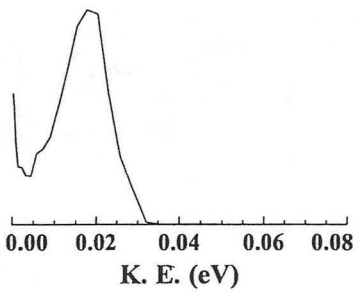
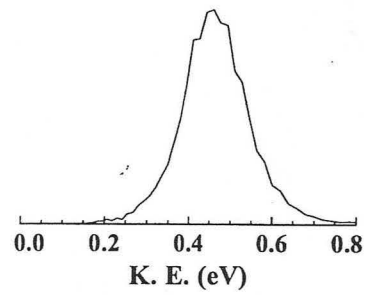
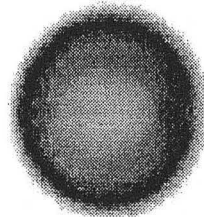
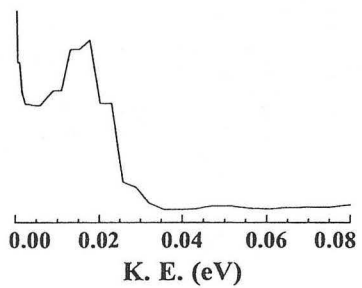
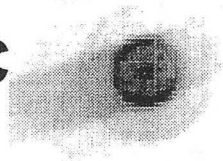
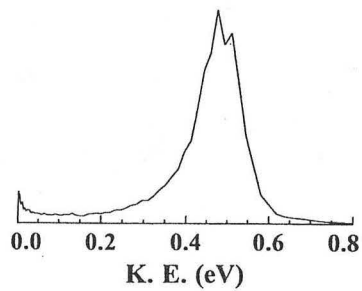
FIGURES

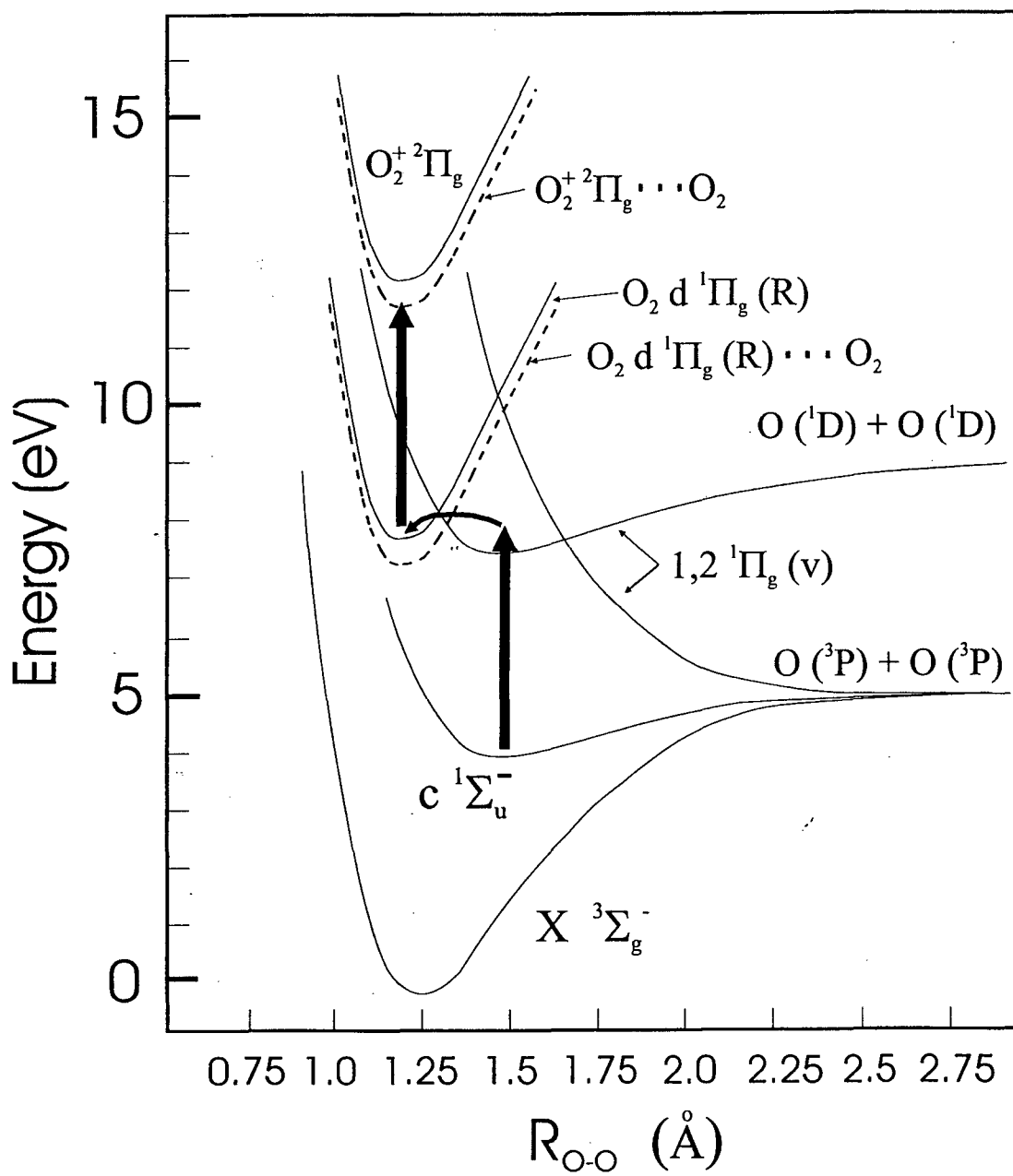
FIG. 1. Raw O_4^+ photoion yield and total photoelectron yield spectra. Expanded region of electron spectrum is shown in inset.

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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