

# Unraveling the mysteries of metastable $O_4^*$

Darcy S. Peterka, Musahid Ahmed, and Arthur G. Suits<sup>a)</sup>

*Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory,  
Berkeley, California 94720*

Kenneth J. Wilson, Anatoli Korokin, Marcel Nooijen, and Rodney J. Bartlett

*Quantum Theory Project, University of Florida, Gainesville, Florida 32611*

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A recent report from our laboratory described 1+1 resonant photoionization spectra of an energetic, metastable  $O_4$  species produced in a dc discharge [Bevsek *et al.*, *Faraday Discuss.* **108**, 131 (1998)]. 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  $c(^1\Sigma_u^-)$  state, which is excited via an allowed transition to the  $1(^1\Pi_g)$  valence state. The latter then couples to the  $d(^1\Pi_g)$  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  $1(^1\Pi_g) \leftarrow c(^1\Sigma_u^-)$  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)]. © 1999 American Institute of Physics. [S0021-9606(99)01613-X]

Interest in tetraoxygen molecules dates to a 1924 paper by G. N. Lewis;<sup>1</sup> since then, studies of  $O_2$  dimers have enjoyed a long history of investigation.<sup>2–4</sup> Theoretical studies of covalently bound  $O_4$  species began with Adamantides’ 1980 prediction<sup>5</sup> of a bound cyclic ( $D_{2d}$ ) form. This stimulated considerable further theoretical effort as this cyclic  $O_4$ , nearly 4 eV higher in energy than two  $O_2$  molecules, appeared to be a promising candidate for a high energy density material.<sup>6–8</sup> Subsequent theoretical studies have also identified a  $D_{3h}$  form analogous to  $SO_3$  at a somewhat higher energy.<sup>9,10</sup> Although experimentalists have long observed evidence of van der Waals’ complexes of ground state  $O_2$  molecules, no evidence has been found supporting the theoretical predictions of covalent  $O_4$  species. In a recent report from our laboratory, 1+1 resonant photoionization spectra were reported for an energetic, metastable  $O_4$  species produced in a dc discharge.<sup>11</sup> 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  $O_2+O_2$ , as well as the existence of a higher excited state through which the ionization takes place. In the absence of plausible alternative accounting for all the observations, an energetic covalent  $O_4$  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  $O_2$  molecule and one in the metastable  $c(^1\Sigma_u^-)$  state.

The experiment<sup>11,12</sup> consists in passing a pulsed molecular beam of oxygen through electrodes held at ground and

$\pm 3$ –5 kV 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  $0.08\text{ cm}^{-1}$ . The laser and molecular beams cross on the axis of a time-of-flight mass spectrometer with velocity map imaging<sup>13</sup> (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 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  $m/e=64$ ,  $O_4^+$  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 vs 6 W). 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  $O_4^+$ . The 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  $3.2$ – $3.6\text{ cm}^{-1}$ . Similar

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: agsuits@lbl.gov

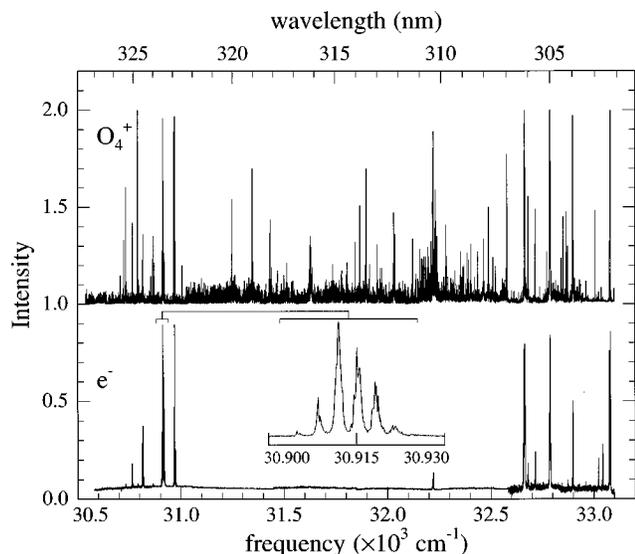


FIG. 1. Raw  $O_4^+$  photoion yield and total photoelectron yield spectra. Expanded region of the electron spectrum is shown in the inset.

rotational structure is also apparent on some lines in the 306 nm region, although not as pronounced.

Photoionization spectra have been recorded using the VELMI technique<sup>13</sup> on many of these resonant lines. Typical images and the corresponding electron kinetic energy 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. In general, these are all very near threshold (less than 50 meV). Occasionally some multiple peaks and some broader peaks are seen, particularly on the lines occurring in the region between 290 and 298 nm.

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  $O_2$  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 programs system.<sup>14</sup> We use a TZ2P basis of Cartesian Gaussians contracted as  $(11s6p3d)/[5s3p2d]$ <sup>15</sup> except as indicated. Table I presents computed coupled-cluster single double (CCSD) and coupled-cluster single double triple [CCSD(T)]<sup>16,17</sup> 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. We also obtained detailed structures and vibrational frequencies for these two species, which are available to interested parties. Included in Table I are the IP-EOM-CCSD<sup>16,17</sup> vertical ionization potentials for the two covalent forms. The lowest IPs 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. Also shown in Table I are the energies of the ionized van der Waals complexes: our result of 11.95 eV is in excellent agreement with the 11.67 eV complete active space self-consistent field (CASSCF) value of Lindh and Barnes.<sup>18</sup> Also presented in Table I are rotational constants for these species. These are

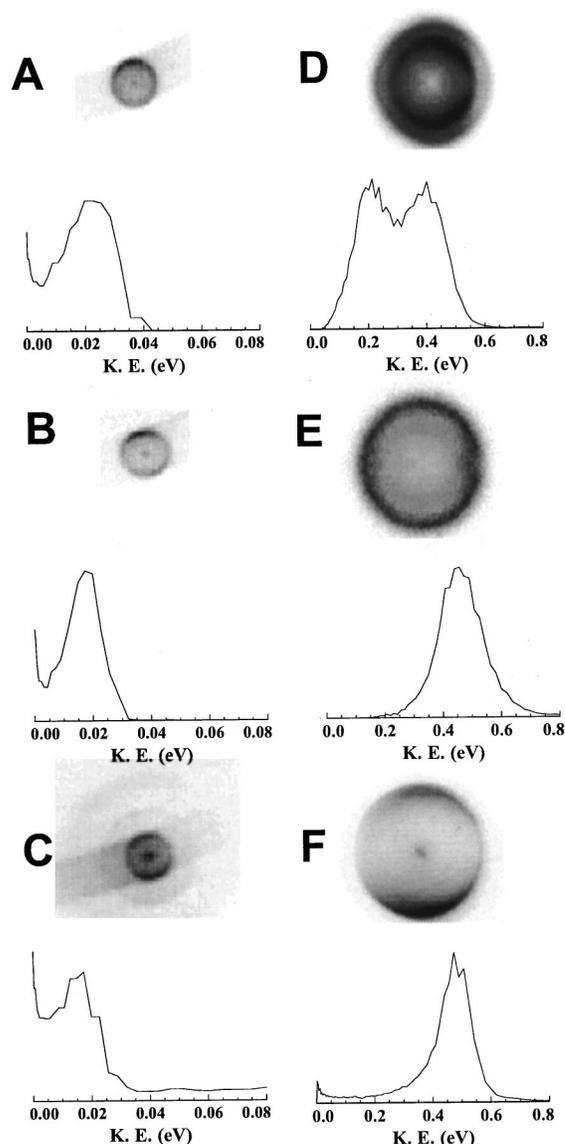


FIG. 2. Photoelectron images and electron kinetic energy release distributions for several resonant lines of  $O_4^+$ . Wavelengths are (a) 323.478 nm, (B) 306.122 nm, (C) 304.987 nm, (D) 296.788 nm, (E) 294.893 nm, and (F) 282.836 nm.

not consistent with the rotationally resolved spectra in the inset in Fig. 1. Even accounting for the nuclear spin symmetry for the  $D_{3h}$  species, a line spacing on the order of  $6B_e$  or  $1.2 \text{ cm}^{-1}$  is the largest expected.

The other question pertains to the existence of a bound excited state of the covalent species and whose vibrational frequencies have been previously estimated.<sup>11</sup> STEOM-CC<sup>19</sup> calculations in the POL1 basis<sup>15</sup> 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 9.2 and 10.0 eV. For the  $D_{3h}$  form, the first state is a forbidden  $A_1''$  which occurs at 7.24 eV with a strong  $E'$  state at 8.92 eV, with the next (dipole forbidden)  $E'$  state at 12.95 eV. There are five triplet states in the range of 6–9

TABLE I. Computed CCSD and CCSD(T) relative energies and rotational constants at optimal geometries for  $O_4$  species. The relative energies, in units of electron volts, are with respect to  $O_2 X(^3\Sigma_g^-) + O_2 X(^3\Sigma_g^-)$  and rotational constants are from CCSD(T) geometries in  $cm^{-1}$ . Also shown are the lowest vertical ionization potentials for the two covalently bound forms of  $O_4$ . The nuclear geometry for these calculations was the optimized CCSD(T)/TZ2P for the ground state.

|          |   | CCSD  | CCSD(T) | Rotational constants | (Be)  | IP    |
|----------|---|-------|---------|----------------------|-------|-------|
| Covalent | $^1A_1 D_{2d}$                            | 4.36  | 5.30    | 0.254 0.478          | 0.478 | 10.98 |
|          | $^2B_{2u} D_{4h}$ ionized state           | 15.14 | 15.89   | 0.260 0.520          | 0.520 |       |
|          | $^1A_1' D_{3h}$                           | 5.66  | 6.52    | 0.204 0.408          | 0.408 | 12.47 |
|          | $^1A_2 C_{3v}$ excited state <sup>a</sup> | 6.46  |         | 0.208 0.406          | 0.406 |       |
|          | $^4A_2 C_{3v}$ ionized state              | 17.39 | 18.49   | 0.194 0.368          | 0.368 |       |
| vdW      | $^4B_u C_{2h}$ ionized state              | 11.67 | 11.95   | 0.149 0.185          | 0.769 |       |
|          | $^4B_{1g} D_{2h}$ ionized state           | 11.67 | 11.95   | 0.149 0.185          | 0.769 |       |

<sup>a</sup>For this species, rotational constants are from the EE-EOM-CCSD geometry.

eV of 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 7.60. However, despite extensive effort, when optimizing the geometry for excited states either with CCSD when applicable, or EOM-CCSD analytical gradient techniques<sup>20</sup> otherwise to determine if there are bound excited states, only two were found: one singlet and one triplet. Neither the energies (shown in Table I) nor the frequencies make a persuasive case for this being the possible intermediate state in the 1+1 experiment. 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,<sup>21</sup> adapted from van der Zande *et al.*<sup>22,23</sup> This is the only species that may possess an allowed optical transition in the wavelength region: there exists an excited  $1(^1\Pi_g)$  state very near the energy of our probe transition, i.e., about 4 eV above this  $c$  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 illuminating series of experiments<sup>22,23</sup> 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 “diabatic” picture, as shown; the  $1(^1\Pi_g)$  level is 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 the Franck–Condon factors connecting it with the ground state of the ion are negligible. In fact, the experiments of van der Zande and co-workers 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. This shows a path to ionization in this wavelength region via the valence–Rydberg interactions. These considerations yield the following 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 (and an  $O_2$  molecule), 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

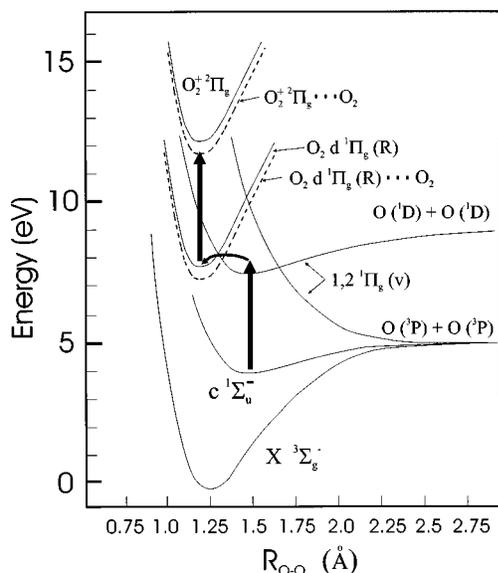


FIG. 3. Relevant potential curves adapted from Ref. 23, from calculations of Ref. 21. The Rydberg and ion curves, duplicated and offset  $-0.45$  eV (the energy of the  $O_2-O_2^+$  bond) are shown as dashed lines (see the text).

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 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 provides a reasonable explanation for the absence of the  $O_2^+$  in these experiments despite the likelihood that the number density of free  $O_2$   $c(1^1\Sigma_u^-)$  molecules is much greater than those involved in complexes. The fate of the free  $O_2$ , upon excitation to the  $1(1^1\Pi_g)$  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  $3.5\text{ cm}^{-1}$ , is very near  $4B_e$  for the  $c(1^1\Sigma_u^-)$  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  $d(1^1\Pi_g)$  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.<sup>24</sup> 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  $800\text{ cm}^{-1}$  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  $O_2 X(3^1\Sigma_g^-)-O_2 1(1^1\Pi_g)$  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  $800\text{ cm}^{-1}$ ; the vibrational frequency in the  $1(1^1\Pi_g)$  state is likely to be similar.

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

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