

COMMENTS

Comment on “Unraveling the mysteries of metastable O_4^* ” [J. Chem. Phys. 110, 6095 (1999)]

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Peterka *et al.* reported in a Communication [J. Chem. Phys. **110**, 6095 (1999)] experimental studies of the metastable O_4^* molecule produced in a pulsed electric discharge of molecular oxygen. Tetraoxygen, O_4 , is an especially interesting and illusive molecule with theoretically predicted metastable states. In trying to reproduce their results on metastable O_4 we find that signals reported in Peterka *et al.* come from iron atoms (Fe, mass 56) instead of O_4 (mass 64). The iron atoms are generated from the metal ring used in the discharge.

In Ref. 1 a pulsed molecular beam of oxygen passes through electrodes held at ground and ± 3 –5 kV so that a discharge occurs in the collision region of the expanding molecular beam. Radiation from a pulsed tunable dye laser ionizes the molecular beam downstream as it passes through an electrostatic lens configured for velocity map imaging.² Time-of-flight mass gating is used to selectively image the formed O_4^+ and photoelectrons. Using a similar apparatus we were able to reproduce the spectral features, cation, and photoelectron images in the 300–330 nm region as reported in Ref. 1. A cation yield spectrum in the 301–307 nm region from Ref. 1 is shown in Fig. 1(a) for comparison with our measured spectrum in Fig. 1(b). Photoelectron and cation yield spectra from Ref. 1 in the 321–326 nm region are shown in Figs. 2(a) and 2(b), respectively, for comparison with our cation yield spectrum in the same region. Two sample photoelectron images and electron kinetic energy release distributions for resonant excitation at 304.76 nm [peak 11 in Fig. 1(b)] and 305.91 nm [peak 13 in Fig. 1(b)] are shown in Fig. 3. Excellent agreement is found with the same quantities that are reported in Figs. 1 and Fig. 2(B) and 2(C) of Ref. 1, except for a shift of ~ 0.22 nm for all observed peaks. The position of peak 11 in Fig. 1(b), 304.76 nm, was reported in Ref. 1 at 304.99 nm, for example. Our dye laser wavelength was calibrated in the 300–320 nm region using numerous (2+1) resonance-enhanced multiphoton ionization (REMPI) lines of atomic iodine, formed from photodissociation of methyl iodide or I_2 . The time of flight for the cation spectra shown in Figs. 1 and 2 corresponds in our

apparatus, however, to that of mass 56. In Ref. 1 this signal was assigned as O_4^+ (mass 64). Our time-of-flight calibration masses included I, Ar^* , and O_2 in the molecular beam on appropriate REMPI wavelengths in this region. I atoms were produced in the photodissociation of CH_3I , Ar metastable was produced in the discharge.

As in Ref. 1, the laser beam (<0.1 mJ/pulse) was unfocused when obtaining these very strong signal cation and photoelectron signals. The photoelectron yield spectrum is identical to the cation yield spectrum at mass 56, and both are the same using neat oxygen or argon in the molecular beam. We could not detect in the entire spectral region *any* signal at the time of flight corresponding to mass range 61–67, even at the highest sensitivities with a focused laser beam. For mass-56 detection a center-dot (zero kinetic energy) image is always seen, indicating that the signal arises only from a parent ion. Because the cation and photoelectron appearance spectra coincide, both signals must arise from the ionization of a neutral species instead of the photodissociation of a larger ion. This leads us to the conclusion that the species studied by Peterka *et al.* was iron (Fe, mass 56).

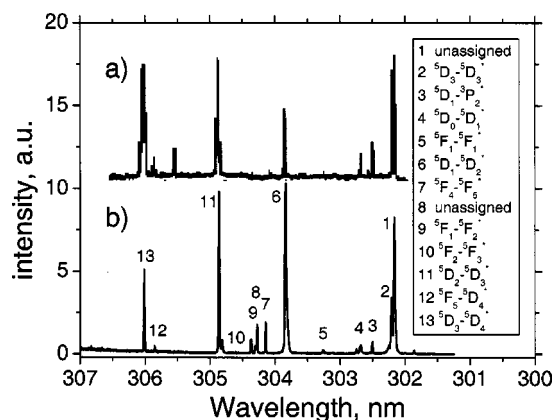


FIG. 1. (a) Appearance spectra in the 300–307 nm region from Ref. 1 for cations at mass 64 in a discharge with molecular beam of O_2 . (b) Our corresponding appearance spectrum using pure Ar in the discharge beam and detection at mass 56. Assignment of the peaks indicated in (b) to known Fe I transitions are listed in the inset table.

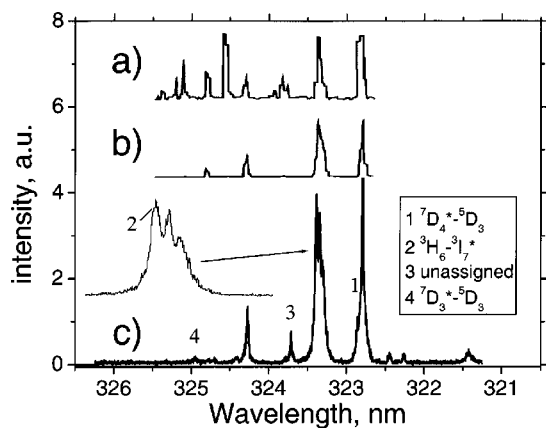


FIG. 2. Appearance spectra in the 321–326 nm region from Ref. 1 for cations at mass 64 (a) and photoelectrons (b) in a discharge beam of O_2 . (c) Our corresponding appearance spectrum using pure Ar in the discharge beam and detection at mass 56. Assignment of the four peaks indicated in (c) to known Fe I transitions are listed in the inset table. A blow up of the region around 323.3 nm is also shown. The first peak in this group, labeled as peak 2, is assigned in the inset table.

We have independently confirmed the presence of ground-state ($3d^6 4s^2 {}^5D$) iron atoms in the discharge beam by a scan of the photon energy in the region of 40 100–40 300 cm^{-1} . Strong peaks due to (1+1) REMPI via the ${}^5D_J - 3d^6({}^5D)4s4p({}^1P^0) {}^5F_J^0$ transitions were observed.

All of the peaks observed in Fig. 1 can be found in the NIST table of Fe emission lines.³ Two of the lines, peaks 1 and 8, are attributed to Fe, but unassigned: the known assignments are listed in Fig. 1. Our wavelength positions agree with the tabulated values³ within 0.01 nm for all peaks. The strongest lines originate from the ground electronic state Fe I $3d^6 4s^2 {}^5D_J (J=0-4)$: levels of the second manifold, $3d^7({}^4F)4s {}^5F_J (J=1-5)$, are also populated. One-photon resonant, two-photon ionization takes place: the strongest lines are resonant with the $3d^7({}^4F)4p {}^5D_J^9 (J=0-4)$ manifold in the 33 000–34 000 cm^{-1} region. The second photon excites the atom above the ionization potential at 63 737 cm^{-1} . As indicated in the photoelectron image kinetic energy distributions shown in Fig. 3, direct ionization into the Fe II $3d^7({}^4F)4p {}^5D_J^9 (J=9/2-7/2)$ manifold results in the strongest, low-kinetic-energy peak. Ionization into Fe II $3d^6({}^5D)4s {}^6D_J (J=9/2-1/2)$ results in higher-energy peaks. These ionization mechanisms are qualitative because the intermediate $3d^7({}^4F)4p {}^5D_J^9 (J=0-4)$ manifold is quite mixed (leading percentages vary from 60% to 40%).

Less than half of the peaks observed in Fig. 2 are found in the Fe NIST emission lines table. It is known that pulsed discharges of this design produce high-energy metastable atoms and molecules.⁴ The unassigned lines are most likely transitions starting from higher-energy metastable states of Fe I, many of which are essentially unknown. With increasing laser intensity and increasing voltage on the discharge more peaks appear in the ion and electron yield spectra, and substantial line broadening takes place. A set of peaks in Fig. 2 (see inset) shows multiple bands, which were interpreted as rotational structure of O_4 in Ref. 1. These peaks are much better resolved in Ref. 1 than in our apparatus. The spacing of the peaks does not change with laser power or electrostatic lens voltage. They correspond in our apparatus, however, to

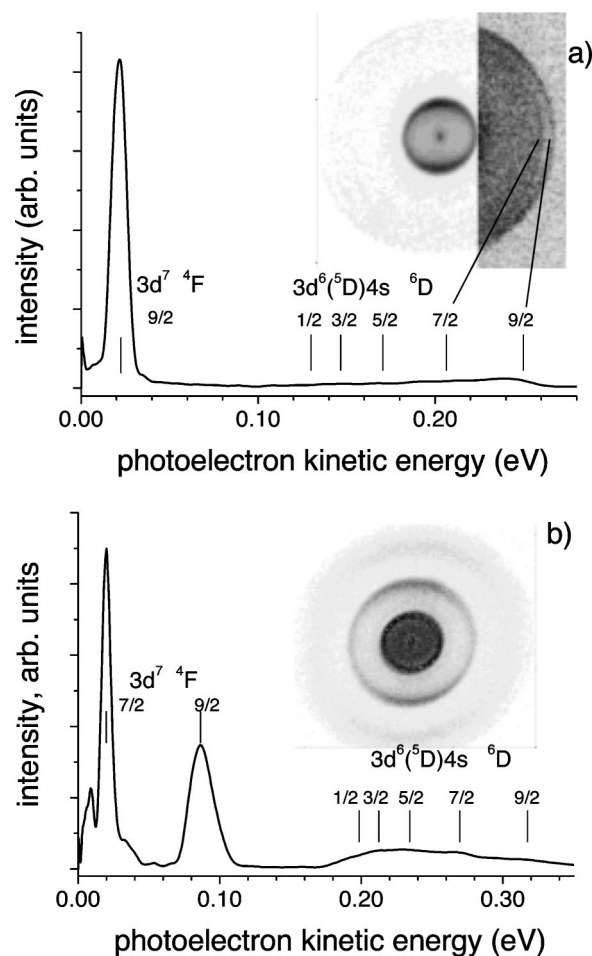


FIG. 3. Velocity map image and kinetic energy release distribution for photoelectrons obtained with the ionization laser resonant at (a) 305.91 nm and (b) 304.76 nm using an Ar discharge beam [peaks 13 and 11 in Fig. 1(b)], respectively. The laser polarization is parallel to the detector face: dark regions correspond to higher signals. Fe II ionization limits are indicated in the figures.

mass 56, not to mass 64. We also observed that a powder of Fe atoms is deposited on the surface of the nozzle during the experiment. This powder can easily be desorbed and entrained in the molecular beam by “shaking” during the normal mechanical operation of the nozzle (as was observed in our experiments) or by laser light, which may explain earlier observations⁵ from the authors of Ref. 1.

The Fe atom signals reported above are coming from the electrodes used to make the discharge. To prove this we replaced the steel wire electrode used in our apparatus with an aluminum electrode. The signals reported here and in Ref. 1 disappeared, and strong Al^+ signals were found when tuning the laser to known (1+1) REMPI lines of ground-state aluminum. Evidence for the formation and photodissociation of oxides incorporating both Fe and Al atoms has been obtained and will be reported in a future study.

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