

## Electron Affinity of Oxygen\*

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(Received 24 March 1965)

**P**HOTODETACHMENT, photoabsorption, and electron attachment experiments are rapidly giving confidence in a value for the electron affinity of oxygen of about 1.47 eV.<sup>1-3</sup> However, ambiguity still exists in the determination of this parameter by electron impact techniques.<sup>4</sup> This note reports a determination of the electron affinity of oxygen using photon impact methods to observe a pair production process.

The technique used in this study consisted of measuring the threshold for the formation of O<sup>+</sup> from O<sub>2</sub> via the process: O<sub>2</sub> + hν = O<sup>+</sup> + O<sup>-</sup>. The threshold law for this type of process has been discussed previously.<sup>5</sup>

The apparatus used, essentially that described previously,<sup>6</sup> was modified along the lines suggested earlier<sup>6</sup> to permit operation with a differentially pumped light source. The Hopfield continuum in helium was used as the source of ionizing radiation. The bandpass (full width at half-maximum) of the ionizing radiation entering the ionization chamber was about 3 Å or approximately 0.07 eV at 700 Å. This bandwidth was chosen as a compromise between ion intensity and monochromator resolution.

The result of this study is shown in Fig. 1. If the Franck-Condon region intersects the dissociation limit of the ion-pair state, one would expect a sharp onset of ionization followed by a slowly varying function due to transitions which occur to the vibrational continuum above the dissociation limit. Ions produced above the dissociation limit will, of course, possess kinetic energy. Figure 1 exhibits a behavior which we believe to be consistent with this interpretation. The breadth of the sharp rise at the onset of ionization reflects the bandpass of the monochromator at the threshold energy and is consistent with a discontinuity at threshold. The slower dropoff above threshold reflects the shape of the Franck-Condon density and the fact that the ion collection efficiency decreases with increasing initial ion kinetic energy.

The true threshold for this process would be the midpoint of the rising portion of the curve if the threshold behavior was a step function equivalent to, in this case, a continuum of δ functions above threshold and would be the peak of the curve if the threshold behavior was an isolated delta function. Clearly, the correct value must lie between these limits, and these limits put a maximum error on the determination. Convolution of the actual resolution function and an excitation function consistent with the cross section above threshold indicates that the correct threshold is at 80% of maximum peak height. Kinetic-energy

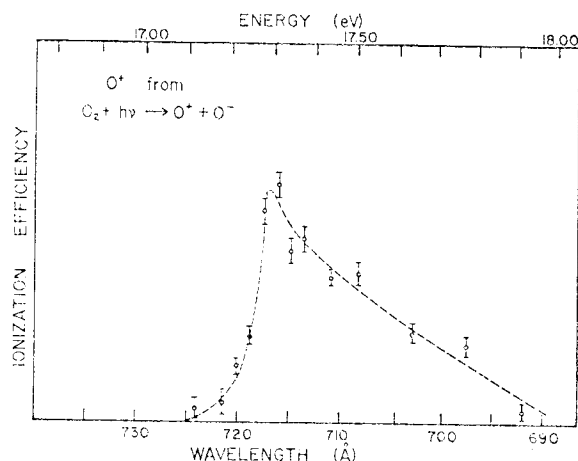


Fig. 1. Photoionization efficiency curve for the process O<sub>2</sub> + hν = O<sup>+</sup> + O<sup>-</sup> as a function of photon energy.

considerations would reduce this slightly. These considerations lead to a value of 717.8 ± 1.0 Å or 17.267 ± 0.024 eV.

The equation relating the threshold of the ion-pair process to the electron affinity of oxygen, E.A.(O), is

$$E.A.(O) = D_0(O_2) + I.P.(O) - A.P.(O^+) + K.E.,$$

where  $D_0(O_2)$  is the dissociation energy of oxygen (5.114 ± 0.002 eV),<sup>7</sup> I.P.(O) is the ionization potential of oxygen (13.614 eV),<sup>8</sup> A.P.(O<sup>+</sup>) is the appearance potential here observed, and K.E. is the kinetic energy of fragmentation which we believe to be zero at the interpreted threshold of Fig. 1. Using the threshold here determined, we obtain E.A.(O) = 1.461 ± 0.024 eV. This value is to be compared with Branscomb's *et al.*,<sup>1</sup> value of 1.465 ± 0.005 and Berry's<sup>2</sup> value of 1.478 ± 0.002. The discrepancy which exists, if any, between our value and those of Branscomb *et al.* and Berry could be due to an error in the value of the dissociation energy of O<sub>2</sub>.

It is clear that the value obtained from impact experiments producing ion pairs is consistent with values obtained by other methods.

\* This work was supported in part by a grant from the National Science Foundation and in part by a grant from the Advanced Research Projects Agency.

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