

ON THE IONIZATION POTENTIAL OF  
MOLECULAR OXYGEN

James A. R. Samson and J. L. Gardner

Behlen Laboratory of Physics

University of Nebraska

Lincoln, NE 68508

ABSTRACT

The ionization potential of  $O_2$  has been measured by the technique of high resolution photoelectron spectroscopy taking into account the influence of rotational structure on the shape of the vibrational bands. A value of  $12.071 \pm .001$  eV ( $1027.1 \pm 0.1 \text{ \AA}$ ) was found for the ionization potential. This value leads to a dissociation energy of  $D_0(O_2^+ X^2\Pi_g) = 6.661 \pm .001$  eV. A lowering of the ionization potential caused by a branch-head when  $\Delta N = -2$  gave an appearance potential for ionization of  $12.068 \pm .001$  eV ( $1027.4 \pm 0.1 \text{ \AA}$ ).

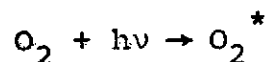
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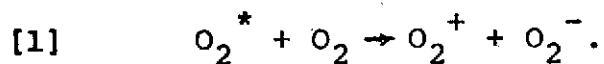
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## INTRODUCTION

An accurate value of the first ionization potential of  $O_2$  has been sought for many years. Because no Rydberg series analysis has been successful in identifying a series limit for the first ionization potential (IP) other techniques have been used. These methods have consisted primarily of electron and photon impact ionization studies. Of these techniques the photoionization method is the more accurate. A major problem of electron and photon impact methods is in indentifying the first appearance of ions. With molecular oxygen ionization can occur at energies less than the first IP (Samson and Cairns 1966) because of the process,



followed by



This process is, of course, pressure dependent. The photo-ionization threshold potential of  $O_2$  was first studied by Inn (1953) who observed ions at photon energies of 12.049 eV. Watanabe and Marmo (1956) also reported ions in this region. They measured a photoionization

yield of 0.7% at 12.028 eV. Ionization at these energies was undoubtedly caused by the high  $O_2$  pressure. However, in the pressure range of a few mTorr process (1) should not be significant. The many results of photoionization, with or without mass analysis, and the use of photoelectron spectroscopy have led to a range of values of the ionization potential between 12.063 and 12.077 eV.

Samson and Cairns (1966) identified the  $v' = 1$  level of  $O_2^+$  ( $X^2\Pi_g$ ) in a photograph of the  $O_2$  absorption bands and this led to a value of 12.063 eV for the IP. This value was lowered when Asundi (1968) and Bhale and Rao (1968) revised the vibrational energy separation between the  $v' = 0$  and  $v' = 1$  levels of the  $O_2^+$  ground level. However, on re-examination of the absorption spectrum it is clear that some ambiguity exists in the identification of the  $v' = 1$  level because of the presence of diffuse absorption lines. Further, in light of high resolution photoelectron spectroscopy giving consistently higher values of the IP it was decided to re-investigate the first ionization potential of  $O_2$  and in particular to try to understand better the effects of rotational levels in lowering the IP and their effect on the photoelectron spectrum. If the IP is lowered because of rotational transitions this would affect the 1966 results.

### Rotational Effects

When a molecular gas is photoionized by a beam of monoenergetic photons from, say, the ground electronic state with  $v'' = 0$  to the ground ionic state with  $v' = 0$  there is not one single ionizing transition but rather a large number of individual transitions between appropriate rotational levels in each state. This is caused by the population of a number of ground state rotational levels at room temperature. Figure 1 shows the percent population of the various rotational levels for  $O_2$  at a temperature of 300 K.

An energy level diagram of  $O_2$  and  $O_2^+$  in their vibrationless ground states is shown in Fig. 2. Photoionization of the neutral molecule is possible from any of the populated rotational levels. Various transitions are shown by the vertical lines. These transitions are grouped into several branches, namely, the O, P, Q, R, and S branches depending on the value of  $\Delta N$  as shown in the Figure.  $N$  is the total angular momentum of the molecule apart from spin. The levels are actually split and these are shown beside the  $J$  numbering of the levels ( $J$  is the total angular momentum including spin). However, the spacings are less than  $2 \text{ cm}^{-1}$  and will not be considered further.

No selection rules for  $\Delta N$  have been enunciated

for the photoionization of  $O_2$ . We assume for the moment that all  $\Delta N$  values are possible.

The ionization potential of a molecule is defined as the energy between the ground state of the neutral and the ion both in their zeroeth vibrational and rotational levels. Let the term value for the transition between these two states be  $\nu_0$ , the band origin, then the term value for a transition from any rotational level  $N''$  of the neutral to a rotational level  $N'$  of the ion is given by

$$[2] \quad \nu = \nu_0 + F'(N') - F''(N'')$$

where  $F(N) = B_0 N(N + 1)$  is the rotational term value and  $B_0$  is the rotational constant for zero vibration. If  $(F' - F'')$  is negative the transition occurs at an energy less than that of the ionization potential. Thus, the true IP is lowered. For  $O_2$ , because the rotational constant  $B'_0$  of the ion is greater than  $B''_0$  of the neutral, a lowering of the IP can only be expected for the P and O-branches for low values of  $N$ . The O-branch actually forms a band head  $22.2 \text{ cm}^{-1}$  below the origin and thus sets a limit to the lowering of the IP (provided there are no additional branches with  $\Delta N = -3, -4, \dots$  etc.  $\Delta N = -3$  has a branch head  $61.4 \text{ cm}^{-1}$  below the origin).

The appearance potential (A.P.) of ions in any

experiment, corrected for instrumental resolution, will be related to the onset of the lowest energy branch. If the 0-branch is present the A.P. will occur  $22.2 \text{ cm}^{-1}$  (2.8 meV) before the true I.P.


The true ionization potential will be determined when the origin is identified.

A vibrational peak in a differential photoelectron spectrum is the integral of the intensities of all the rotational transitions within the vibrational band. The peak maximum will not necessarily occur at the origin. The position of the peak maximum depends on the relative intensities of the various branches within the band. To a first approximation, the intensity of a branch can be calculated by assuming that the transition probabilities of the various rotational transitions are constant. Thus, the intensities will depend only on the population of the rotational levels in the ground state (Figure 1). If the rotational levels, corrected for the Boltzmann distribution, are convoluted with the instrument resolution function of a photoelectron spectrometer the photoelectron vibrational peak should be reproduced. Conversely, the shape of a photoelectron peak should yield the position of the origin when properly de-convoluted. This is similar to the procedure used by Walker *et al.* (1973) in their study of HF.

Thus, the procedure to find the origin is to obtain a high resolution photoelectron spectrum of the  $\nu' = 0$  band of  $O_2^+$  and to compare the shape of that band with that obtained from selected branches whose relative intensities are varied to give the best fit.

## RESULTS

The cylindrical mirror analyzer used to obtain the photoelectron spectrum of  $O_2$  has been described previously (Gardner and Samson 1973). An important feature of the analyzer for the present work is a retarding/accelerating lens to allow analysis of the electrons at a constant pass energy and thereby achieve high resolution. Also the electrons were analyzed at an angle of  $54^\circ 44'$  to eliminate any effects caused by varying angular distributions of the photoelectrons (Samson and Gardner 1972).

The energy scale was calibrated by mixing trace quantities of xenon with the  $O_2$ . The ionization potential of  $Xe(^2P_{3/2})$  is 12.130 eV, which only lies about 60 meV above that of  $O_2$ . Further, the photoelectron peak of Xe provided an excellent instrument  function.

A photoelectron spectrum of  $O_2$  is shown in Fig. 3. Dispersed NeI radiation at  $736 \overset{\circ}{\text{A}}$  was used with an analyzer pass energy of 0.5 eV. The half-width of the  $Xe(^2P_{3/2})$

peak was 9 meV. This illustrates the use of Xe as a calibrating gas. The spin-orbit splitting of each vibrational level into a  ${}^2\Pi_{1/2,3/2}$  doublet, is clearly resolved. A similar spectrum, only of the  $v' = 0$  level, was taken with dispersed ArII radiation at  $919.78 \text{ \AA}$  to give better resolution through reduced Doppler broadening (Fig. 4). The pass energy was 0.3 eV, which gave a resolution of 7.3 meV ( $58 \text{ cm}^{-1}$ ).

The intensity of each rotational line was taken to be proportional to

$$(2N'' + 1)e^{-B''N''(N'' + 1)hc/kT}$$

Each line was then convoluted with a Gaussian instrument function of half-width  $58 \text{ cm}^{-1}$ . Figure 5 shows the resulting distribution of intensity in each of the O, P, Q, R, and S branches for the  ${}^2\Pi_{1/2}$  state. Similar results were obtained for the  ${}^2\Pi_{3/2}$  state. The results were then summed over all rotational levels, for both states, allowing the intensities of each pair of branches (O,S) and (P,R), and Q to vary until a best fit to the experimental data was obtained. The assumption that the branches have equal intensities within each pair appears to be justified, to a first approximation, because in the case of the rotator with  $\Lambda = 0$  the line strengths  $S_N$  for  $\Delta N = +1$  and  $-1$  are, respectively,  $S_N = N + 1$  and



and  $S_N = N$ , with slightly more complicated functions of  $N$  for  $\Delta N = \pm 2$  (Herzberg 1950). The relative intensity of the  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  states was also allowed to vary. The spectroscopic value of  $200 \text{ cm}^{-1}$  for the separation of the  ${}^2\Pi_{1/2,3/2}$  states was used (Krupenie 1972).

The results of this fitting procedure are shown in Fig. 4. The solid line is the calculated photoelectron distribution and the data points are the experimental results. With this fit the band origin is located  $20 \text{ cm}^{-1}$  (2.5 meV) below the peak maximum. The peak maximum is measured experimentally at  $12.073 \pm .001 \text{ meV}$ . Thus, the true ionization potential of  $\text{O}_2$  is  $12.071 \pm .001 \text{ meV}$ .

The experiment was repeated with a pass energy of 0.5 eV giving a resolution of  $69 \text{ cm}^{-1}$ . Again, an excellent fit to the experimental data was obtained. An average of the best fitting parameters gave an intensity for the O and S-branches  $0.57 \pm .05$  times that of the Q-branch intensity. The P and R branches were found to have zero intensity. This suggests a selection rule of  $\Delta N = 0, \pm 2$ . Higher values of  $\Delta N$  were considered but these broadened the peaks more than was observed. The average ratio of the  ${}^2\Pi_{3/2}$  to  ${}^2\Pi_{1/2}$  state was found to be  $0.93 \pm .02$ . This is of the same magnitude as the relative intensity of the spin-orbit components found in the halogens (Frost et.al. 1967).

Because there is a branch head in the O-branch the appearance potential of electrons must be  $22.2 \text{ cm}^{-1}$  (2.8 meV) below the ionization potential. That is, the appearance potential of ionization occurs at an energy of  $12.068 \pm .001 \text{ eV}$ . This is in agreement with the completely independent method of simply taking the energy of the first appearance of electrons (as shown in Fig. 4) and correcting for the analyzer resolution ( $58 \text{ cm}^{-1}$ ).

Ionization potentials obtained from photoelectron spectroscopy data cite the energy of the vibrational peak maximum. As noted earlier this position will not be, in general, the origin of the band. A comparison of high resolution photoelectron spectroscopy data shows close agreement of the energy of the  $v' = 0$  peak maximum. Similarly, there is close agreement in the published values of the first appearance potential of ionization. They lie, on the average, about 6 meV below the photoelectron spectroscopy data. Table 1 summarizes the various data. The consistency of the results in the two categories gives strong support to the present analysis assigning the origin or true ionization potential to a value of 12.071 eV.

Table 2 summarizes the relevant findings of this work.

The  ${}^2\Pi_{1/2,3/2}$  spin-orbit splitting observed in the present work is  $185\text{ cm}^{-1}$  (23 meV). This must represent a lower limit of the splitting because the effect of the unresolved rotational lines is to narrow the separation. This is demonstrated by the solid curve in Fig. 4 that was obtained using the spectroscopic value of  $200\text{ cm}^{-1}$  (24.8 meV) for the  ${}^2\Pi_{1/2,3/2}$  splitting. Thus, unless a vibrational band with spin-orbit splitting is deconvoluted a partially resolved photoelectron spectrum will always underestimate the magnitude of the splitting. In the present case for  $\text{O}_2^+$  the spectroscopic value of  $200\text{ cm}^{-1}$  (24.8 meV) is recommended.

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TABLE 1. Ionization potential (eV) of O<sub>2</sub> by various techniques.

References	Appearance potential	True IP	Photoelectron Spectroscopy (peak max.)
Present Results	12.068 ± .001	12.071 ± .001	12.073 ± .001
a	12.067 ± .010	-	-
b	12.063 ± .010	-	-
c	12.067 ± .001	-	-
d	12.065 ± .003	-	-
e	12.072 ± .008	-	-
f	-	-	12.070 ± .005
g	-	-	12.071 ± .005
h	-	-	12.077
i	-	-	12.075

a,b Samson and Cairns (1966).

c McNeal and Cook (1966).

d Nicholson (1963).

e Dibeler and Walker (1967).

f Turner (1968).

g Edqvist et.al. (1970).

h Dromey et.al. (1973).

i Collin and Natalis (1969).

Note: The AP were obtained from photoionization studies using mass spectrometers (refs. a,e), photo-ionization of O<sub>2</sub> 'Δ (refs. a,c) and ion chambers (refs. b,d).

TABLE 2. Summary of data obtained from the present photoionization study of O<sub>2</sub>.

Ionization potential	12.071 ± .001 eV
Appearance potential	12.068 ± .001 eV
Dissociation energy	6.661 ± .001 eV
$2\Pi_{3/2} : 2\Pi_{1/2}$	0.93 ± 0.01 <sup>a</sup>
(O,S) : Q-branch	0.57 ± 0.02 <sup>a</sup>
(P,R) : Q-branch	0
Selection rule $\Delta N$	0, ±2

<sup>a</sup> Quoted error limits represent the deviations of two independent sets of data.

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### Figure Captions

1. The fraction of molecules in the various rotational levels of the ground state of  $O_2$  ( $v''=0$ ) at a temperature of 300 K.
2. Energy level diagram of  $O_2$  and  $O_2^+$  illustrating transitions between the various rotational levels.
3. Photoelectron spectrum of  $O_2$  photoionized by the monochromatic Ne I resonance line at  $736 \text{ \AA}$ . The first seven vibrational bands are shown including the Xe doublet  $^2P_{1/2,3/2}$  used for calibrating the energy scale. Vibrational bands of the ground state of  $O_2^+$  continue to  $v'=20$ . Analyzer resolution was 9 meV.
4. Photoelectron spectrum of the  $v'=0$  band of  $O_2$  photoionized by the Ar II resonance line at  $920 \text{ \AA}$ . The solid curve is the calculated shape of the band taking into account the rotational structure. The open circles are the experimental data points. Analyzer resolution was 7 meV.
5. Relative intensities of the rotational branches for the transitions  $\Delta N = 0, \pm 1, \text{ and } \pm 2$  assuming a constant transition probability for all rotational lines, a thermal distribution of the rotational lines for  $T = 300 \text{ K}$ , and an instrumental analyzer function of  $58 \text{ cm}^{-1}$  (7 meV). The origin is represented by zero on the abscissa axis.

