Forbidden Electron Attachment in O₂

By

H. Sambe and D. E. Ramaker

Prepared for Publication
in the

Physical Review B

George Washington University
Department of Chemistry
Washington, D.C. 20052

December, 1988

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.
Forbidden Electron Attachment in O₂ (Uncl.)

The electron stimulated desorption yield from condensed O₂ exhibits three peaks around 7, 8.5, and 13 eV, while that from O₂ gas shows only the 7-eV peak. The 7-eV peak is known to arise from the O₂(1Σ⁺→1Σ⁰)₂⁺ compound state. In this paper, the 8.5- and 13-eV peaks are shown to arise from the O₂(3Σ⁺→1Σ⁰)₂⁺ and O₂(2Σ⁺→1Σ⁰)₂⁺ compound states, respectively.

The absence of the 8.5- and 13-eV peaks in the gas-phase spectrum is shown to be due to a 1Σ⁺→1Σ⁰ selection rule, which is valid only in the highly symmetric environment of the gas phase.
I. INTRODUCTION

In collisions of electrons with molecules, an electron may be attached to a molecule forming a temporary negative ion or a negative compound state. The production of this compound state is governed by certain selection rules. The selection rules are:

1. An allowed compound state must have either $1S-1/2$ or $1S+1/2$ total spin, when the target molecule has total spin $S$;
2. it should have an electronic configuration which differs by less than three-electron excitations with respect to the initial state (i.e., the target molecule plus an incident electron);
3. it must not have $\Sigma^+$ (or $\Sigma^-$) symmetry, if the target molecule is linear and has $\Pi^-$ (or $\Pi^+$) symmetry. The last selection rule has been established just recently and has been called the $\sigma^-$ selection rule. When either of the three selection rules are not satisfied, we use the term, forbidden electron attachment, by analogy with forbidden optical transitions.

Compound states which are forbidden in the gas phase may not be forbidden in the solid phase, because of distortion of the local symmetry. Although the selection rules involving spin symmetry and number of electron excitations may persist in the solid phase, the rule involving cylindrical symmetry of linear molecules (or the $\sigma^-$ selection rule) may relax in the solid phase. In fact, this breakdown of cylindrical symmetry has been clearly observed in optical transitions. In this paper, we study oxygen molecular systems in the gas and solid phases and
identify, for the first time, the compound states which are
forbidden by the $^3S$ selection rule. \( \Omega_{^3S} \neq 0 \)

In Sec. II, we analyze some experimental data previously
published in the literature. Our findings are summarized in
Table I. In Sec. III, various properties of the lower-lying $O_2$-
compound states are predicted utilizing empirical methods. These
properties are summarized in Table VII. In Sec. IV, we identify
the forbidden compound states by comparing experimental (Table I)
and theoretical (Table VII) results. Finally in Sec. V, we
review previous work.

II. EXPERIMENTAL RESULTS

A. Energy dependence of the $O^-$ yields

Figure 1 shows electron stimulated $O^-$ desorption yields from
various samples ($O_2/W$, $O_2/Pt$, and $O_2$ gas) as a function of the
incident electron energy. These $O^-$ yield curves are reproduced
from figures previously published in the literature.\(^3\)-\(^5\) The
relative magnitudes of these curves do not represent the actual
relative $O^-$ yields. For example, the $O^-$ yield from $O_2$ gas
(dotted curve) is arbitrarily normalized to the peak of the $O_2/Pt$
curve for comparison. For the $O_2/W$ data,\(^6\) a polycrystalline $W$
ribbon was dosed with 10 L (Langmuirs, 1L=10\(^{-6}\) Torr Sec) of $O_2$
at room temperature. All three $O_2/Pt$ samples\(^7\)-\(^9\) were prepared by
condensing $O_2$ gas on a polycrystalline Pt ribbon at 20 K with a
constant $O_2$ dosage. The estimated $O_2$ film thickness is 3
monolayers (ML) for all three Pt samples. Two of the three

[Table]

**Quality Inspected**

**Avail and/or Special**

A-1
curves for O$_2$/Pt are measured with retarding potentials ($V_{\text{m}}=-1.5$ and -1.8 eV) against the outgoing O$^-$ ions. The $V_{\text{m}}=-1.8$ eV retarding potential, for example, discriminates O$^-$ ions whose kinetic energies outside the condensed film are less than 1.8 eV.

The shaded area shows our estimated contribution due to the direct process, which we shall discuss later. Figure 2 shows the OH$^-$ yield from C$_6$H$_{14}$ (IML)/O$_2$ (3ML)/Pt and the O$_2$.O$^-$ and O$_2$ yields from (O$_2$)$_n$ cluster. These curves are reproduced from Refs. 6 and 7 respectively. The O$^-$ yield from O$_2$ gas (dotted curve) is shown again for comparison.

The O$^-$ ions from O$_2$ are generated by the reaction

$$e^- + O_2 \rightarrow O_2^- \rightarrow O + O^- \ , \ (1)$$

so that maxima in the O$^-$ yield curve reflect the positions of O$_2^-$ compound states. The OH$^-$ yields from C$_6$H$_{14}$ (IML)/O$_2$ also reflect the positions of O$_2^-$ compound states, because the OH$^-$ ions are generated by two steps; namely, reaction (1) followed by

$$O^- + C_6H_{14} \rightarrow OH^- + C_6H_{13}^- \ , \ (2)$$

according to Sanche and Parenteau. Similarly, O$_2$.O$^-$ and O$_2$ ions from O$_2$ clusters are generated via the initial step,

$$e^- + (O_2)_n \rightarrow (O_2)_{n-1}.O_2^- \ . \ (3)$$

Therefore, the O$_2$.O$^-$ and O$_2$ yield curves also reflect the positions of O$_2^-$ compound states.
Figures 1 and 2 exhibit three peaks around 7, 8.5, and 13 eV as indicated in the two figures. The 8.5-eV peak in (O\(_2\))\(_n\) curves (Fig. 2) has been interpreted as a shift of the 7-eV state due to the polarization of the (O\(_2\))\(_n\) cluster.\(^7\) Also the 8.5-eV peak in O\(_2\)/Pt curves (Fig. 1) was not ascribed to another compound state.\(^8\) In this work, we attribute the 8.5-eV peak to another O\(_2\)\(^-\) compound state, based on the following four reasons: (1) Any polarization of the (O\(_2\))\(_n\) clusters should shift the 7-eV peak to lower energy, contrary to that observed. (2) The peak position of the 8.5-eV feature does not shift to higher energy, when the retarding potential is increased from -1.5 to -1.8 eV. In addition, there is an indication of a shoulder around 7 eV in the O\(_2\)/Pt(V\(_n\)=1.5eV) curves, suggesting that the 7-eV peak has not been shifted. (3) All ion-yield curves measured without retarding potentials, except the O\(^-\) yield curve from gaseous O\(_2\), indicate the presence of the 8.5-eV feature. In fact, the 8.5-eV feature dominates in the O\(_2\)\(^-\)-(O\(_2\))\(_n\) curve of Fig. 2. (4) Theory predicts three O\(_2\)\(^-\) compound states in the energy range from 7 to 15 eV, which can dissociate into an O+O\(^-\) limit. To sum up, the 7-, 8.5-, and 13-eV features we believe to arise from three different O\(_2\)\(^-\) compound states.

As seen in Figs. 1 and 2, the relative intensities of the three features depend strongly on the structure of the sample (such as the O\(_2\) layer thickness, substrate, and cluster size), the detected ions (O\(^-\), O\(_2\)\(^-\), O\(_2\)O\(^-\), or OH\(^-\)), and the detection angle of the ions. However, to establish the nature of the forbidden electron attachment, analysis of these intensities is
not essential. The only fact which is used in this work is that both the 8.5- and 13-eV features are absent (or negligible relative to the 7-eV feature) in the 0- yield curve of gaseous D$_2$ (see Figs. 1 and 2).

B. 0- kinetic energy distributions

Figure 3 shows the kinetic energy distributions of the 0- ions from D$_2$ (3ML)/Pt measured at various incident electron energies ($E_e$=5.7, 7.7, 12, and 13 eV). These data were obtained by Azria et al. with an electron-energy resolution of 0.3 eV and an ion-energy resolution of 0.5 eV. The relative 0- kinetic energy ($E_{\text{rel}}$) (the absolute scale of the 0- kinetic energy was not determined) is measured with respect to the peak energy of the $E_e$=5.7eV curve. The three symbols in horizontal bars (closed and open circles and open triangle) indicate three different contributions, which will be described later. The horizontal bar with a symbol indicates the possible range of the peak position for each contribution. In Fig. 4, these peak-position ranges are plotted as a function of the incident electron energy, $E_e$. The broken straight lines are given by the equation,

$$E_{\text{rel}} = (E_e - E_d)/2 - 1.03 \text{ (eV)},$$

(4)

where $E_d$ is the relevant O+O- dissociation limit measured from the O$_2$ ground state ($v=0$). The $E_d$=5.65, 5.62, and 7.84 eV correspond to the lowest three dissociation limits, O($^3\Pi$)+O$^-(\tilde{F})$, O($^1\Sigma$)+O$^-(\tilde{F})$, and O($^1\Sigma$)+O$^-(\tilde{P})$, respectively. The O- kinetic energy ($E_{\text{rel}}$) from D$_2$ gas is given by
\[ E_{\text{ave}} = \frac{(E_i - E_o)}{2}, \]  
where \( E_i \) and \( E_o \) have the same meanings as those of Eq. (4). The constant shift (1.03 eV) of \( E_{\text{ave}} \) with respect to \( E_{\text{ave}} \) arises from the artificial choice of the zero of energy for \( E_{\text{ave}} \) (i.e., \( E_{\text{ave}} = 0 \) for \( E_i = 5.7 \text{eV} \) and \( E_o = 3.65 \text{eV} \)).

As seen in Fig. 4, the features denoted by closed circles fit well on the straight line with \( E_o = 3.65 \text{eV} \), indicating that they arise from the process,

\[ e^- + O_2(3P) \rightarrow O_2^- \rightarrow O(3P) + O^- (3P). \]  
Similarly, the features with open circles fit well on the line with \( E_o = 5.62 \text{eV} \), indicating that they arise from the process,

\[ e^- + O_2(3P) \rightarrow O_2^- \rightarrow O(3P) + O^- (3P). \]  
On the other hand, the features with open triangles do not fit on any of the lines. These features have been previously ascribed to the multiple scattering process, that is,

\[ e^- + O_2(3P) \rightarrow O_2^- \rightarrow O(3P) + e^- \]  
followed by

\[ e^- + O_2(3P) \rightarrow O_2^- \rightarrow O(3P) + O^- (3P). \]  
The above analysis supports this interpretation. A good fit to theory for the closed and open circles suggests that no significant amount of momentum is transferred to the \( O_2 \) lattice when the \( O^- \) desorbs from the surface. A similar conclusion was reached in the study of \( \text{Cl}^- \) desorption from condensed \( \text{Cl}_2 \).
The $O^-$ kinetic energy distributions (Fig. 3) give information on the dissociation limits of the three $O_2^-$ compound states. The curves at $E_1=12$ and 13 eV show that the 13-eV compound state dissociates into the lowest two limits and the probability for dissociation into the second lowest limit is larger than that into the first. The $E_1=7.7$ eV curve shows that the 7-eV compound state dissociates only into the lowest limit. The dissociation limits of the 8.5-eV compound state cannot be obtained directly from Fig. 3; however, it can be deduced by the following argument. The 7-eV compound state yields predominantly 1.7-eV (=(7.0-3.65)/2) $O^-$ ions, provided that the momentum transfer to the $O_2$ lattice is negligible. The retarding potential $V_r=-1.5$ eV is strong enough to discriminate such low-energy ions, and indeed the 7-eV peak disappears in the $V_r=-1.5$ eV curve (see Fig. 1). Similarly, if the 8.5-eV compound state predominantly dissociates into the second lowest limit, the dominant $O^-$ kinetic energy would be 1.5 eV (=(8.5-5.62)/2). The retarding potential $V_r=-1.5$ eV should discriminate such low-energy $O^-$ ions. The presence of the 8.5-eV peak in the $V_r=-1.5$ eV curve (Fig. 1), therefore, indicates that the 8.5-eV compound state predominantly dissociates into the lowest limit.

C. Widths

The widths of the 8.5- and 13-eV features can be estimated from the curves in Figs. 1 and 2. From the $O_2/\text{Pt}(V_r=-1.5$ and -1.8 eV) curves in Fig. 1, we estimate FWHMs for the 8.5- and 13-eV features to be 2.3±0.4 and 2.1±0.4 eV, respectively. In these
estimates, the energy spread of the electron beam (0.3 eV) has been taken into account. From the 8.5-eV feature in the $O_2^-/(O_2)^+$ curve and the 13-eV feature in the DH+/C$_6$H$_4$/O$_2$ curve, we estimate their FWHMs to be 2.2±0.3 and 2.3±0.4 eV, respectively. The energy spreads of the electron beams in these experiments are 0.5 eV (Ref. 7) and 0.3 eV (Ref. 6) respectively. The two estimates (i.e., 2.3 and 2.2 eV for the 8.5-eV feature and 2.1 and 2.3 eV for the 13-eV feature) agree reasonably well.

We can estimate the contribution of a compound state to the $O^-$ yield curve utilizing its FWHM. The shaded area in Fig. 1 shows such a contribution estimated with a FWHM=2.1 eV and the electron beam spread=0.3 eV for the 13-eV feature. Figure 1 indicates a slowly varying background under the 13-eV feature. This background is due to multiple-electron scattering and is expected to vary slowly. We have already seen the presence of multiple-electron scattering in the $O^-$ kinetic energy distribution (Fig. 3), namely the contributions marked with open triangles. The multiple-electron scattering in Fig. 3 is about 50% at 13 eV, which agrees with the background contribution (about 50%) at 13 eV in Fig. 1. This agreement supports the FWHM=2.1 eV estimate for the width of the 13-eV compound state.

In conclusion, we estimate the widths of the 8.5- and 13-eV features to be 2.2±0.3 and 2.1±0.4 eV, respectively. The width of the 7-eV feature, which is observed in the $O^-$ yield curve of O$_2$ gas, is 2.0±0.2 (Refs. 3 and 9).

D. Summary
Table I summarizes the observed characteristics of the 7-, 8.5-, and 13-eV compound states. For all three states, the survival rate against autodetachment (i.e., $D_e^- \rightarrow D_0^+e^-$) during dissociation into an $O^+O^-$ limit must be substantial, because $O^-$ ions from these three compound states are observed. The vertical energies in the table are measured from the $D_0$ ground state ($v=0$) to the peaks observed in the ion yield curves. The FWHMs are the widths observed in the ion yield curves. The "I," "II," and "III" in the "Dissociation limit" column stand for the lowest and the second lowest $O^+O^-$ dissociation limits. In the following sections, we shall identify these three compound states using their characteristics listed here.

III. THEORETICAL ANALYSES

A. Vertical energies

Tables II, III, and IV list the observed and estimated vertical energies measured from the $D_0$ ground state to the $D_e$, $D_0^-$, and $D_e^-$ valence states, respectively. The valence states are identified by their electronic configurations (EC) and state symmetries except for the three $D_e^- (1s^-1s^-) \pi \pi \nu$ states, which have an additional label, I, II, or III. When a valence state mixes strongly with Rydberg states, such as the $D_e^- (1s^-1s^-) \pi \pi \nu$ valence state with the $\pi \pi \nu (1s^-1s^-3p_0)$ Rydberg state, the pure valence state energy is estimated from analyses presented in the literature. All the vertical energies listed in the three tables represent pure valence state energies. The references on which
the experimental data or analyses are based are cited in the tables.

In these three tables, estimated (as opposed to observed) vertical energies are enclosed in parentheses. Table V shows how we estimate an unobserved vertical energy from theoretical calculations, using the $O_x^{-1}(l_x u^{-1})^2P_u(II)$ state as an example. Although theoretical calculations may not accurately reproduce the absolute energy splittings arising from a given electronic configuration, they usually reproduce the relative energy splittings, as shown in Table V (compare the "Experiment" and "Theory" columns). In other words, when a scale factor is included and optimized such that the scaled energies reproduce the observed splittings as closely as possible, we usually obtain excellent agreement with experiment. Adopting the estimated splitting 4.1 eV for $O_x^{-1}(l_x u^{-1})^2P_u(II)$—$O_x^{-1}(l_x u^{-1})^2P_u$, and the observed energy 16.70 eV for the $O_x^{-1}(l_x u^{-1})^2P_u$ state, we estimate the $O_x^{-1}(l_x u^{-1})^2P_u(II)$ state energy to be 20.8 eV. This estimated energy is listed in Table III and enclosed in parentheses. The theoretical calculations utilized are cited in the "Reference" columns. When theoretical calculations are not available, such as for the $2e_x^{-1}$ and $2e_x^{-1}1t_g$ cases, we use the relative energies of analogous ECs, such as $3e_x^{-1}$ and $3e_x^{-1}1t_g$, for the above examples.

The configuration center (CC) of an electronic configuration (EC) is defined as a weighted average of state energies arising from the EC. Tables II, III, and IV include such CCs, which are
calculated from the vertical energies. The averaged vertical excitation energy (AVEE) can be calculated from a pair of CCs. For example, the AVEE for the $1s_u-1s_v$ excitation can be calculated from the differences of the following three pairs: $O_6^--1s_u-1s_v$ and $O_6^--1s_u-1s_v$ and the GSC (the ground state configuration of $O_6$), or $O_6^--1s_u-1s_v$ and $1s_u$. Table VI compares the AVEEs calculated from the different pairs of CCs. This comparison clearly shows that the AVEEs are nearly independent of the molecular charge. Assuming this independence, we can often predict the CCs of $O_6^-$ states with an uncertainty of less than 1 eV.

We expect the charge independence in the AVEE's based on the following argument. The CC of an EC specified by a set of electron occupation numbers $(n_1,n_2,...)$ is given to a good approximation by

$$E_{cc}(n_1,n_2,...) = A + \sum_i B_i n_i + \sum_{i,j} C_{ij} n_i n_j ,$$

where $A$, $B_i$, and $C_{ij}$ are independent of occupation numbers. The quadratic coefficients $C_{ij}$ are symmetric with exchange of indexes and approximately satisfy the relation

$$C_{ij} = (C_{ij} + C_{ji})/2 .$$

Further, the diagonal coefficients $C_{ii}$ are approximately proportional to

$$C_{ii} \propto \int \phi_1^*(r_1) \left( \frac{1}{|r_1-r_2|} \right) \phi_1^*(r_2) r_1^2 dr_1 dr_2 ,$$
where \( \Psi_i(r) \) is the \( i \)-th molecular orbital (MO). Using Eqs. (10) and (11), we have the AVEE for the 1\rightarrow2 excitation,

\[
E_{\text{ave}}(n_{1-1},n_{2+1},\cdots) - E_{\text{ave}}(n_{1},n_{2},\cdots) = B_{2} - B_{1} + (C_{22} - C_{11})E_{1}\, \text{(13)}
\]

Expression (13) shows that the AVEE should depend on \( E_{1}n_{1} \) or the total charge of a molecule, which is a sum of nuclear charges minus \( E_{1}n_{1} \). For homonuclear diatomic molecules, however, we have \( C_{11} = C_{22} \) to a very good approximation among valence MOs \( I \) and \( J \), because the Coulomb integral, Eq. (12), is insensitive to the details of the \( \Psi_i(r) \) distribution, and because \( \Psi_i(r) \) for valence MOs in a homonuclear diatomic molecule are similar in size and localization. Hence, for a valence excitation of homonuclear diatomic molecules, we should have

\[
E_{\text{ave}}(n_{1-1},n_{2+1},\cdots) - E_{\text{ave}}(n_{1},n_{2},\cdots) = B_{2} - B_{1} \, \text{(14)}
\]

This explains the near independence on molecular charge and justifies the use of the AVEEs for predicting other unobserved \( D_{a}^- \) states.

There are several ways to estimate the unobserved vertical energies of the \( D_{a}^- \) compound states. For example, we can estimate the vertical CC of the \( 3\sigma_{a}^-1\sigma_{a}^\pi \) configuration from any of the following three equations,

\[
3\sigma_{a}^-1\sigma_{a}^\pi - 1\sigma_{a} (0.2 \text{ eV}) = 7.5 \text{ eV} \, \text{(15)}
\]
\[
3\sigma_{a}^-1\sigma_{a}^\pi - 1\sigma_{a} - 1\pi_{a}^\sigma (7.8 \text{ eV}) = 0.6 \text{ eV} \, \text{(16)}
\]
\[
3\sigma_{a}^-1\sigma_{a}^\pi - 3\pi_{a} (10.6 \text{ eV}) = -2.5 \text{ eV} \, \text{(17)}
\]
where the right hand sides of the above equations are the AVEEs for $O_\text{a}$ listed in Table VI. Although we could use the AVEEs for $O_\text{a}^-$ instead of $O_\text{a}$, we prefer the $O_\text{a}$ data to the $O_\text{a}^-$ data because the total charge difference between $O_\text{a}$ and $O_\text{a}^-$ is smaller than that between $O_\text{a}^-$ and $O_\text{a}^-$. These equations give the $3o_a^- - 1s_a^+$ energy as 7.7, 8.4, and 8.1 eV, respectively. Averaging these three, we estimate the $3o_a^- - 1s_a^+$ energy to be 8.1 eV with a probable uncertainty of ±0.9 eV. This and similarly estimated vertical energies for the lower-lying $O_\text{a}^-$ valence states are listed in Table VII. The listed ECs are the lowest 7; the next lowest EC is located around 24 eV.

We have excluded $O_\text{a}^-\text{Rydberg states}$, that is the $v^-\text{Ryd}^-$ states, from our considerations for the 8.5- and 13-eV compound states, because Rydberg states are not observed in the solid phase and probably do not exist in the solid. Even if the $O_\text{a}^-\text{Rydberg states}$ do exist in the solid, they most likely do not dissociate into an $O^+\text{-}O^-\text{limit}$. In any event, we find that some of our estimated $O_\text{a}^-\text{valence states}$ agree nicely with the 8.5- and 13-eV features observed in the $O^-$ yields. In the following sections, we restrict ourselves to the $O_\text{a}^-\text{valence states}$.

### B. Properties of the $O_\text{a}^-\text{valence states}$

Table VII summarizes the properties of the lower-lying $O_\text{a}^-\text{valence states}$. We explain each property in the following subsections.

#### 1. Electron attachment
According to the selection rules described in Sec. I, we can classify electron attachments into three categories: allowed with one-electron excitation (A(1)), allowed with two-electron excitations (A(2)), and forbidden (F). The attachment probability of A(1) excitations generally much higher than that of A(2). The possible lower-energy-electron attachments from the \( \Omega \) ground state \( ^{2}S_{\text{u}}^{-} \) are classified as above and listed in Table VII. Although the formation of the \( ^{3}A_{\text{u}}(3S_{\text{u}}) \) state appears to be A(1), it is not A(1) but A(2) because the \( ^{3}A_{\text{u}}(3S_{\text{u}}) \) state arises from the \( ^{1}S_{\text{g}}(^{3}A_{\text{u}})3S_{\text{u}} \) configuration but the initial state has the \( ^{1}S_{\text{g}}(^{3}E_{\text{g}})6S_{\text{g}} \) configuration. Here, \( \ell \Delta_{\text{u}} \) represents an incoming electron orbital of kinetic energy \( \ell \) and symmetry \( \Delta_{\text{u}} \). All forbidden attachments in the table are due to the \( \ell - \sigma \) selection rule. These \( \ell - \sigma \) forbidden attachments are expected to relax in the solid phase; the analogous \( \ell - \sigma \) forbidden photoabsorption processes are indeed observed in solid \( \Omega \).

2. Electron detachment

Figure 5 illustrates a dissociative attachment process accompanied with autodetachment or autoionization, also called electron detachment. The \( \Omega^{-} \) state, which is formed by electron impact of energy \( \ell \), autoionizes into an \( \Omega_{\text{a}} \) state, when \( W^{-}(R) > W(R) \) or \( R_{a} < R < R_{c} \). Here, \( W^{-}(R) \) and \( W(R) \) are the potential energy curves of the \( \Omega_{\text{a}}^{-} \) and \( \Omega_{\text{a}} \) states, \( R_{a} \) is the turning point of the \( W^{-}(R) \) at the energy \( \ell \), and \( R_{c} \) is the crossing point of the two potential curves (see Fig. 5). In order to dissociate into
an O+O\textsuperscript{-} limit, the O\textsubscript{2}\textsuperscript{-} state must survive against the above-mentioned autoionization. According to Bardseley et al.,\textsuperscript{29} the dissociative attachment cross section \( \sigma_{AA}(E) \) for the above process is given approximately by

\[
\sigma_{AA}(E) = \sigma_{AA}(E) \exp\left(-\int_{R_c}^{\infty} \Gamma(R)/\mathcal{A}v(R) \, dR \right), \tag{18}
\]

where \( \sigma_{AA}(E) \) is the cross section for formation of the O\textsubscript{2}\textsuperscript{-} state; \( \Gamma(R) \) is the width of the O\textsubscript{2}\textsuperscript{-} state with respect to the autoionization; and \( v(R) \) is the relative velocity of the nuclei. The exponential factor in Eq. (18) represents the probability that the O\textsubscript{2}\textsuperscript{-} state survives against the autoionization.

\( \Gamma(R) \) for one-electron processes, such as

\[
\text{O}_2^{-}(1s_u^{-1}1s_g)\text{e}^{-} \rightarrow \text{O}_2(1s_u^{-1}1s_g)^{-}\text{e}^+ + \text{e}^{-}, \tag{19}
\]

is governed by the kinetic energy of the outgoing electron \( (\Delta W(R) = W^{-}(R) - W(R)) \) and the asymptotic angular momentum \( j \) of the outgoing electron through the centrifugal barrier. For small \( \Delta W \), \( \Gamma \) is proportional to

\[
\Gamma \propto \Delta W^{\frac{j+1}{2}}, \tag{20}
\]

for a one-electron process, and, in general, \( \Gamma \) increases monotonically with \( \Delta W \).\textsuperscript{29} For two-electron processes, on the other hand, \( \Gamma \) is a slowly varying function of \( \Delta W \) and is orders of magnitude smaller than that for one-electron processes, except for the \( \Delta W \ll 1 \) case. Since the survival factor depends exponentially on \( \Gamma \) (Eq. (18)), the survival factor for one-electron processes is several orders of magnitude smaller than
that for two-electron processes except again for the $\Delta W \ll 1$
case.

The magnitude for autoionization via one-electron processes
can be characterized by a pair of parameters, $\Delta W(R_e)$ and $\Delta R_{\text{ee}}$
($=R_0-R_e$), where $R_e$ is the equilibrium internuclear distance for
the $0^+_1$ ground state. Both parameters are referred to $R_e$ because
the initial $0^+_1$ state is formed with the highest probability at
$R=R_e$ according to the Franck-Condon principle. The larger the
$\Delta W(R_e)$ and $\Delta R_{\text{ee}}$, the smaller the $e_{\text{OA}}$ (or $O^-$ yield). These $\Delta W(R_e)$
and $\Delta R_{\text{ee}}$ parameters are listed in Table VII.

There are two types of states in Table VII: those which
autoionize by detaching the $1s_\pi$ electron and those by detaching
the $3\sigma_u$ electron. The states in the former group have much
smaller $\Delta W(R_e)$ and $\Delta R_{\text{ee}}$ than those in the latter group. The $0^-_{\text{O}_2^-}(3\sigma_u)^2 \Sigma_u^-$ state, one of the latter group, dominates the
vibrational excitation spectra. This state, however, does not
appear in the $0^-$ yield curve, indicating that the survival rate
of this state is negligibly small. Other states in the latter
group also should have negligible survival rates, since they have
larger $\Delta W(R_e)$ and $\Delta R_{\text{ee}}$ than the $0^-_{\text{O}_2^-}(3\sigma_u)^2 \Sigma_u^-$ state. In short,
all states which autoionize by detaching the $3\sigma_u$ electron cannot
appear in the $0^-$ yield curve. On the other hand, the $0^-_{\text{O}_2^-}(1s_\pi^-$
$3\sigma_u)^2 \Pi_u$ state, one of the former group, has been observed in
the $0^-$ yield curve, indicating that the survival rate of this
state is substantial. Since other states in the former group
have smaller $\Delta W(R_e)$ and $\Delta R_{\text{ee}}$ than this state, they should have
even larger survival rates. In other words, all states which autoionize by detaching the 1s_e electron, except for the Os^-
(1s_e)π_u state, can produce O^- ions if they are formed. The Os^-
(1s_e)π_u state cannot produce O^- ions, because its vertical
energy (0.21 eV) is much lower than the lowest O2O^- dissociation
limit (3.65 eV). In conclusion, the survival rate analyses
indicate that only three O^- states, π_u(1s_e-W_1s_u^-), π_u(2s_e-
1s_u^-), and π_u(2s_e-1s_u^-), can produce ample O^- ions.

Figure 6 schematically shows σ_a(E), σ_a(E), and SF(E)
(survival factor) as a function of the incident electron energy
E. σ_a(E) has a peak at E=W_(R_π) because of the Franck-Condon
principle. SF(E) is unity below E=W_(R_π), since r=0 in this
region, and decreases monotonically with increasing E, since the
integrand of the survival factor is always positive and the lower
integration limit (R_π) decreases with increasing E (see Eq.
(18)). Since σ_a(E)=σ_a(E)SF(E), the peak position of σ_a(E)
should be shifted to lower energy relative to that of σ_a(E).
This means that a peak position observed in the O^- yield (a_π peak)
should be lower than the corresponding vertical energy (the σ_a peak).
Indeed, the O^- yield peak observed at 6.7 eV,
which is due to the Os^-(1s_u^-1s_e^-)π_u resonance, is lower than
the vertical energy 7.8 eV by 1.1 eV. For the Os^-(2s_e-
1s_e^-)π_u^- and Os^-(2s_e^-1s_u^-)π_u^- resonances, we expect smaller
shifts (< 0.3 eV) than for the Os^-(1s_u^-1s_e^-)π_u resonance,
because the former two states have smaller ΔW(R_π) and ΔR_π
parameters than the latter state.
3. Franck-Condon widths

The width of the repulsive \( D_m^- \) compound state is predominantly governed by the Franck-Condon overlap integral between the \( v=0 \) vibrational wavefunction of the \( D_m^- \) ground state, \( \psi_0(R) \), and the vibrational wavefunction of the repulsive \( D_m^- \) compound state. In the reflection approximation,\(^{28,29}\) the repulsive wavefunction can be replaced by a \( \delta \) function which differs from zero only at the classical turning point. The results obtained with this replacement, deviate only slightly from those obtained with accurate wavefunctions.\(^{28,29}\) With this approximation, the Franck-Condon width (FCW) of the repulsive \( D_m^- \) compound states can be given,

\[
\text{FCW} = 4R(u=0) \times \left| \frac{dW^-(R)}{dR} \right|_{R=R_m^-},
\]

where \( 4R(u=0) \) is the FWHM of \( \psi_0(R)^2 \), because \( W^-(R) \) of a repulsive state is nearly linear over the Franck-Condon region.

The FCWs in Table VII are estimated from theoretical calculations in the literature, except for the FCW of the \( ^3\Pi_u^- (1\sigma_u^- 1\sigma_u^+) \) state. The FCW of this state is calculated from the experimental slope determined by O'Malley.\(^{30,31}\) The slopes (i.e., \( dW^-(R)/dR \) at \( R=R_m^- \)) for the \( ^3\Pi_u^- (1\sigma_u^-) \), \( ^3\Sigma_u^- (3\sigma_u) \), and \( ^3\Sigma_u^- (5\sigma_u) \) states are calculated from the MCSCF results\(^{28,29}\) by quadratic curve fittings. The data in parentheses are estimated by assuming empirical relations such as

\[
\text{Slope}(3\sigma_u^- 1\sigma_u^+) - \text{Slope}(1\sigma_u^- 1\sigma_u^+) = \text{Slope}(5\sigma_u^- 1\sigma_u^+) - \text{Slope}(1\sigma_u^- 1\sigma_u^+). \tag{22}
\]
The error ranges for the FCWs (2.4 and 2.2 eV) of the \( ^{3}I_{u}^{-}(5\sigma_{u}^{-}+1\pi_{u}^{-}) \) and \( ^{3}I_{u}^{-}(2\sigma_{v}^{-}+1\pi_{u}^{-}) \) states may be around ±0.4 eV.

There are two experiments which reflect the FCWs. First, the vibrational excitation cross section for \( v=1-4 \) show a single peak with FWHM of 5.0 eV, which has been attributed to the \( 0\pi_{u}^{-}(3\sigma_{u}^{-})^{3}I_{u}^{-} \) resonance. The FWHM (5.0 eV) of the vibrational cross section should be larger than that (4.3 eV) of the electron attachment, supporting our estimate of 4.3 eV. Second, the \( O^{-} \) yield due to the \( 0\pi_{u}^{-}(1\sigma_{v}^{-}+1\pi_{u}^{-})^{3}I_{u}^{-} \) resonance has a FWHM of 2.0 eV. The difference between the FWHM (2.0 eV) of the \( O^{-} \) yield and the FCW (3.0 eV) of this compound state is caused by a sizable autodetachment rate (see Fig. 6). Since autodetachment from the \( 0\pi_{u}^{-}(3\sigma_{u}^{-}+1\pi_{u}^{-})^{3}I_{u}^{-} \) and \( 0\pi_{u}^{-}(2\sigma_{v}^{-}+1\pi_{u}^{-})^{3}I_{u}^{-} \) compound states should be much smaller than that from the \( 0\pi_{u}^{-}(1\sigma_{v}^{-}+1\pi_{u}^{-})^{3}I_{u}^{-} \) state, the FWHMs of these two compound states in the \( O^{-} \) yield curve should be close to their FCWs.

4. Dissociation limit

The dissociation limits of the lower-lying \( 0\pi_{u}^{-} \) valence states can be determined by the non-crossing rule. The molecular states resulting from the two lowest dissociation limits of \( 0\pi_{u}^{-} \), known from Wigner-Witmer rules, are listed in Table VIII. According to the non-crossing rule, these molecular states must be connected to the \( 0\pi_{u}^{-} \) valence states with the same symmetry without crossing each other. This implies, for example, that the lowest \( ^{3}I_{u}^{-} \) valence state must be connected to the lowest limit and the second lowest \( ^{3}I_{u}^{-} \) valence state to the second lowest
limit. Another example, both the lowest two $^2\Pi_u$ valence states must be connected to the lowest limit and the lowest $^2\Pi_u$ valence state to the second lowest limit. Dissociation limits determined as above are listed in Table VII, where "1" and "2" denote the lowest and the second lowest dissociation limits respectively.

Figure 7 shows schematically the potential curves for some of the $O_2^-$ valence states. These curves are drawn based on the data in Table VII (such as the vertical energy, FCH, and dissociation limit) and two theoretical calculations,\superscript{3f-3h} which were carried out only for large internuclear distances ($R > 1.6 \text{ Å}$). The apparent avoided curve crossing between the two $^5\Sigma_u^+$ curves is predicted by both calculations. This curve crossing suggests that the $^5\Sigma_u^+$(1) state formed at the Franck-Condon region may end up with the second lowest O-O^- limit.

IV. IDENTIFICATION OF THE O$_2^-$ COMPOUND STATES

Comparing Tables I and VII, we identify the 7-, 8.5, and 13-eV $O_2^-$ compound states to arise from the $^4\Pi_u(1\Sigma_u^-1\Sigma_u^+)$, $^2\Sigma_u^+(3\Sigma_u^-1\Sigma_u^+)$, and $^2\Sigma_u^+(2\Pi_u^-1\Sigma_u^+)$ states, respectively. Almost every aspect (vertical energy, electron attachment probability in the gas phase, survival rate against autodetachment, Franck-Condon broadening, and dissociation limit) supports and confirms these identifications. Moreover, we can exclude alternative identifications: We can exclude the $O_2^-$ $(1\Sigma_u^-)^2\Pi_u$ state, because its vertical energy is much lower than the lowest O-O^- limit. The $O_2^-$ states arising from the $3\Pi_u$, $1\Sigma_u^-$, $^3\Pi_u3\Pi_u$, and $3\Pi_u^-1\Sigma_u^+$ configurations have survival rates which
are too small to yield O\textsuperscript{-} ions and FCIs which are too large for the observed line widths. Furthermore, states from the last two ECs have vertical energies which are too high to be any of the three features. Hence, we conclude that the 8.5- and 13-ev features are due to the O\textsubscript{2}-(3\textpi\textsubscript{a}^-\text{1\textpi\textsubscript{b}}\textsuperscript{a})\textsuperscript{1\textpi\textsubscript{b}} and O\textsubscript{2}-(2\textpi\textsubscript{a}^-\text{1\textpi\textsubscript{b}}\textsuperscript{a})\textsuperscript{2\textpi\textsubscript{a}} compound states. This identification implies that the absence of these features in the gas phase is due to the \(\sigma\) selection rule.

V. PREVIOUS INTERPRETATIONS

The 8.5- and 13-ev features have been interpreted previously. Xiang and Lichtman,\textsuperscript{a} who reported the O\textsuperscript{-} yield curve from O\textsubscript{2}/W (Fig. 1), attributed the 13-ev peak to the O\textsubscript{2}-(3\textpi\textsubscript{a}^-\text{1\textpi\textsubscript{b}}\textsuperscript{a})\textsuperscript{1\textpi\textsubscript{b}} state, or the "7-ev" state, which was regarded as shifted because of a substrate effect. They overlooked a weak 8.5-ev feature in their spectrum. Sanche and co-workers,\textsuperscript{b,c} who reported the three O\textsuperscript{-} yield curves from O\textsubscript{2}/Pt (Fig. 1) and the OH\textsuperscript{-}/O\textsubscript{2}/Pt spectrum in Fig. 2, assigned the O\textsubscript{2}-(3\textpi\textsubscript{a}^-\text{1\textpi\textsubscript{b}}\textsuperscript{a})\textsuperscript{1\textpi\textsubscript{b}} state (that is, the "8.5-ev" state) to the 13-ev feature. Further, the absence of the 13-ev feature in the gas-phase spectrum was attributed to the angular dependence rule given by Dunn,\textsuperscript{d} rather than to the \(\sigma\) selection rule.\textsuperscript{e} Hörk et al.,\textsuperscript{f} who reported the O\textsubscript{2} and O\textsubscript{2} yields from (O\textsubscript{2})\textsubscript{n} clusters (Fig. 2), attributed both the 7-ev and 8.5-ev features to the O\textsubscript{2}-(3\textpi\textsubscript{a}^-\text{1\textpi\textsubscript{b}}\textsuperscript{a})\textsuperscript{1\textpi\textsubscript{b}} state. Our analyses in this work do not support any of the above interpretations.
Acknowledgments

We greatly acknowledge fruitful cooperation with Dr. L. Sanché's group. This work was partially supported by the Office of Naval Research.
References


<table>
<thead>
<tr>
<th>Name</th>
<th>Vertical energy from ground state (eV)</th>
<th>O^- yield</th>
<th>Survival rate</th>
<th>FWHM (eV)</th>
<th>Dissociation limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;7-eV&quot;</td>
<td>6.7</td>
<td>large</td>
<td>large</td>
<td>2.0±0.1</td>
<td>&quot;1&quot;</td>
</tr>
<tr>
<td>&quot;8.5-eV&quot;</td>
<td>8 - 9</td>
<td>negligible</td>
<td>large</td>
<td>2.7±0.3</td>
<td>&quot;1&quot;</td>
</tr>
<tr>
<td>&quot;13-eV&quot;</td>
<td>13</td>
<td>negligible</td>
<td>large</td>
<td>2.4±0.3</td>
<td>&quot;2&quot;</td>
</tr>
</tbody>
</table>

*From the O_2 ground state to peak positions in the O^- yield curves.*

*Survival rate against autodetachment.*

*Widths observed in the ion yield curves.*

*"1" and "2" denote the lowest and the second lowest O+O^- dissociation limits.*
TABLE II. Observed and estimated vertical energies (eV) of the lower-lying D_2 states. Estimated energies are enclosed in parentheses.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Configuration center (eV)</th>
<th>State symmetry</th>
<th>Vertical energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>0.60</td>
<td>^aD_e^-</td>
<td>0.00</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bD_e^-</td>
<td>0.98</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^cD_e^-</td>
<td>1.43</td>
<td>10</td>
</tr>
<tr>
<td>1e_u^-1e_u</td>
<td>7.5</td>
<td>^aE_u^-</td>
<td>5.8</td>
<td>10, 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bE_u^-</td>
<td>6.0</td>
<td>10, 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^cE_u^-</td>
<td>6.1</td>
<td>10, 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^dE_u^-</td>
<td>8.5</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^eE_u^- (10.8)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>^fE_u^- (12.6)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>3e_u^-1e_u</td>
<td>8.1</td>
<td>^aE_u</td>
<td>7.7</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bE_u (9.2)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>1e_u^-3e_u</td>
<td>10.6</td>
<td>^aE_u</td>
<td>10.2</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bE_u (11.9)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>2e_u^-1e_u</td>
<td>14.3</td>
<td>^aE_u</td>
<td>14.2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bE_u (14.6)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>2e_u^-1e_u</td>
<td>28.9 ± 1.0</td>
<td>^aE_u</td>
<td>28.5 ± 1.0</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^bE_u (30.0)^*</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated from the splitting energies of the 3e_u^-1e_u states.
TABLE III. Observed and estimated vertical energies (eV) of the lower-lying $O_{2}^{-}$ states. Estimated energies are enclosed in parentheses.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Configuration center (eV)</th>
<th>State symmetry</th>
<th>Vertical energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\pi_{u}^{-1}$</td>
<td>12.31</td>
<td>$\pi_{g}$</td>
<td>12.31</td>
<td>17</td>
</tr>
<tr>
<td>$1\pi_{u}^{-1}$</td>
<td>19.2</td>
<td>$\pi_{u}(I)$</td>
<td>16.70</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi_{u}(II)$</td>
<td>17.73</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi_{u}(III)$</td>
<td>19.1</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi_{u}(III)$</td>
<td>(20.8)</td>
<td>19</td>
</tr>
<tr>
<td>$3\sigma_{g}^{-1}$</td>
<td>19.6</td>
<td>$\alpha_{g}^{-}$</td>
<td>18.17</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{g}^{-}$</td>
<td>19.40</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{g}^{-}$</td>
<td>20.43</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_{g}^{-}$</td>
<td>(20.8)</td>
<td>18</td>
</tr>
<tr>
<td>$2\sigma_{u}^{-1}$</td>
<td>25.9</td>
<td>$\sigma_{u}^{-}$</td>
<td>24.58</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{u}^{-}$</td>
<td>(26.0)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{u}^{-}$</td>
<td>(26.8)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{u}^{-}$</td>
<td>27.3</td>
<td>20</td>
</tr>
<tr>
<td>$2\sigma_{e}^{-1}$</td>
<td>40.0</td>
<td>$\sigma_{e}^{-}$</td>
<td>38.8</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{e}^{-}$</td>
<td>(40.3)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{e}^{-}$</td>
<td>(40.8)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{e}^{-}$</td>
<td>(41.1)</td>
<td>21</td>
</tr>
</tbody>
</table>

*The energy scale is shifted by 0.8 eV to make the first-peak energy position agree with the accurate energy 12.3 eV.

*Estimated from the splitting energies of the $3\sigma_{g}^{-1}$ states.
TABLE IV. Observed and estimated vertical energies (eV) of the lower-lying $O_2^-$ states. Estimated energies are enclosed in parentheses.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Configuration center (eV)</th>
<th>State symmetry</th>
<th>Vertical energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\pi_e$</td>
<td>0.21</td>
<td>$\pi\sigma$</td>
<td>0.21</td>
<td>22</td>
</tr>
<tr>
<td>$1\pi_\gamma - 1\pi_e$</td>
<td>7.8 ± 0.2</td>
<td>$\pi\sigma$</td>
<td>7.8 ± 0.2</td>
<td>23$^a$</td>
</tr>
<tr>
<td>$3\delta_\gamma$</td>
<td>10.6 ± 0.3</td>
<td>$\Sigma^-$</td>
<td>9.5 ± 0.3</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta^-$</td>
<td></td>
<td>23$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Sigma^-$</td>
<td></td>
<td>23$^a$</td>
</tr>
</tbody>
</table>

$^a$The uncertainty indicates the sensitivity of the fitting and thus does not reflect absolute errors.

$^b$Estimated from the splitting energies of the $2\pi^-\Gamma$ states.

$^c$Estimated using the $\Sigma^--\Sigma^-$ energy difference calculated by MCSCF with 85 configurations.
### TABLE V. Energy splittings (eV) of the $0_u^+(1s_0^{-1})$ states.

The scaled energies are obtained from the unscaled energies by multiplying with a constant factor. This factor is chosen so that the scaled energies reproduce experimental energy splittings as well as possible.

<table>
<thead>
<tr>
<th>State</th>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Scaled</td>
</tr>
<tr>
<td>$^1P_u$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$^3P_u(I)$</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>$^3P_u$</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>$^3P_u(II)$</td>
<td>---</td>
<td>4.1</td>
</tr>
<tr>
<td>$^3P_u(III)$</td>
<td>7.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>
TABLE VI. Comparison of averaged vertical excitation energies (eV).

<table>
<thead>
<tr>
<th>Excitation</th>
<th>$0^+_{x}$</th>
<th>$D_{x}$</th>
<th>$0^+_{x}^{*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1z_u \rightarrow 1z_o$</td>
<td>6.9 ((1z_u^{-1}1z_o^{-1}))</td>
<td>6.9 ((1z_u^{-1}1z_o^{-1}-\text{GSC}))</td>
<td>7.6 ± 0.2 ((1z_u^{-1}1z_o^{-1}-1z_o))</td>
</tr>
<tr>
<td>$3z_o \rightarrow 1z_o$</td>
<td>7.3 ((3z_o^{-1}1z_o^{-1}))</td>
<td>7.3 ((3z_o^{-1}1z_o^{-1}-\text{GSC}))</td>
<td>---</td>
</tr>
<tr>
<td>$1z_o \rightarrow 3z_o$</td>
<td>---</td>
<td>---</td>
<td>10.4 ± 0.3 ((3z_o^{-1}1z_o^{-1}))</td>
</tr>
<tr>
<td>$2z_u \rightarrow 1z_o$</td>
<td>13.6 ((2z_u^{-1}1z_o^{-1}))</td>
<td>13.7 ((2z_u^{-1}1z_o^{-1}-\text{GSC}))</td>
<td>---</td>
</tr>
<tr>
<td>$2z_o \rightarrow 1z_o$</td>
<td>27.7 ((2z_o^{-1}1z_o^{-1}))</td>
<td>28. ((2z_o^{-1}1z_o^{-1}-\text{GSC}))</td>
<td>---</td>
</tr>
</tbody>
</table>
TABLE VII. Properties of the lower-lying $D_{2}$ valence states.

<table>
<thead>
<tr>
<th>Electronic Symmetry configuration</th>
<th>Vertical energy (eV)</th>
<th>Electron attachment (eV)</th>
<th>$\Delta R$ (Å)</th>
<th>Width (eV)</th>
<th>Dissociation limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\sigma_{g}$</td>
<td>$\eta_{u}$</td>
<td>0.21</td>
<td>A(1)</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>$1\sigma_{u}^{-1}1\sigma_{g}^{+}$</td>
<td>$\eta_{u}$</td>
<td>7.8 ± 0.2</td>
<td>A(2)</td>
<td>1.8</td>
<td>0.18</td>
</tr>
<tr>
<td>$3\sigma_{g}^{-1}1\sigma_{g}^{+}$</td>
<td>$\eta_{u}$</td>
<td>8.1 ± 0.9</td>
<td>F</td>
<td>(0.4)</td>
<td>(0.04)</td>
</tr>
<tr>
<td>$2\sigma_{u}^{-1}1\sigma_{u}^{+}$</td>
<td>$\eta_{u}$</td>
<td>14.3 ± 0.9</td>
<td>F</td>
<td>(0.1)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>$3\sigma_{u}$</td>
<td>$\eta_{u}$</td>
<td>9.5 ± 0.3</td>
<td>A(1)</td>
<td>9.6</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>$\eta_{u}$</td>
<td>10.7 ± 0.5</td>
<td>A(2)</td>
<td>9.8</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>$\eta_{u}$</td>
<td>11.5 ± 0.5</td>
<td>F</td>
<td>10.0</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>$\eta_{u}$</td>
<td>11.9 ± 0.4</td>
<td>A(1)</td>
<td>12.0</td>
<td>0.59</td>
</tr>
<tr>
<td>$1\sigma_{u}^{-1}1\sigma_{g}3\sigma_{g}^{-1}1\sigma_{g}^{+}$</td>
<td>$\eta_{u}$</td>
<td>17.5 ± 1.0</td>
<td>A(2)</td>
<td>(10.0)</td>
<td>(0.4)</td>
</tr>
<tr>
<td></td>
<td>$\eta_{u}$</td>
<td>18.1 ± 1.0</td>
<td>A(2)</td>
<td>(10.0)</td>
<td>(0.4)</td>
</tr>
</tbody>
</table>

* $\eta_{u}$ represents the lower-lying $D_{2}$ valence state.
TABLE VIII. Dissociation limits of the $\text{O}_2^-$ valence states which have the lower energies in the Franck-Condon region.

<table>
<thead>
<tr>
<th>Dissociation limit</th>
<th>Molecular states belonging to the dissociation limit</th>
<th>$\text{O}_2^-$ valence state</th>
<th>Symmetry</th>
<th>Electronic configuration</th>
<th>Vertical energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^-(\Pi_b) + 0^+(\Pi_a)$</td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Pi_b(1)$</td>
<td>$\Sigma_g$</td>
<td>$1\pi_a$</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Pi_b(1)$</td>
<td>$\Sigma_g$</td>
<td>$1\pi_a^{-1}1\sigma_a^-$</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Sigma_g$</td>
<td>$\Omega_c(1)$</td>
<td>$3\sigma_a^{-1}1\pi_a$</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Pi_b(1)$</td>
<td>$\Sigma_g$</td>
<td>$3\sigma_u$</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Pi_b(1)$</td>
<td>$\Sigma_g$</td>
<td>$3\sigma_u$</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Sigma_g$</td>
<td>$\Omega_c(1)$</td>
<td>$3\sigma_u$</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>$\Pi_b^-(2), \Sigma_g^-$</td>
<td>$\Pi_b(1)$</td>
<td>$\Omega_c$</td>
<td>$3\sigma_u$</td>
<td>11.9</td>
</tr>
<tr>
<td>$0^-(\Pi_u) + 0^+(\Sigma_a)$</td>
<td>$\Pi_u^-(2), \Sigma_u^-(2)$</td>
<td>$\Pi_u(1)$</td>
<td>$\Sigma_u^{-1}$</td>
<td>$2\sigma_u^{-1}1\pi_a$</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>$\Pi_u^-(2), \Sigma_u^-(2)$</td>
<td>$\Pi_u(1)$</td>
<td>$\Sigma_u^{-1}$</td>
<td>$1\pi_a^{-1}3\sigma_u$</td>
<td>17</td>
</tr>
</tbody>
</table>
Figure captions

FIG. 1. Previously reported electron stimulated O⁻ desorption yields from O₂/W (Ref. 4), O₂/Pt (Refs. 5 and 6), and O₂ gas (Ref. 3) are plotted as a function of the incident electron energy. Vᵣ denotes the retarding potential applied to the outgoing O⁻ ions. The shaded area shows our estimated contribution due to the direct process. The vertical dot-dash lines indicate the probable peak positions of the involved O₂⁻ compound states.

FIG. 2. Previously reported electron stimulated negative ion (O⁻, O₂⁻, O₃⁻, or OH⁻) desorption yields from O₂ gas (Ref. 3), O₅P clusters (Ref. 7), or C₆H₅/O₂/Pt (Ref. 6). The negative ion yields are plotted as a function of the incident electron energy. The vertical dot-dash lines indicate the probable peak positions of the involved O₂⁻ compound states.

FIG. 3. Kinetic energy distributions of the O⁻ ions from O₂(3ML)/Pt (Ref. 5), which are measured at various incident electron energies, Eᵣ=5.7, 7.7, 12, and 15 eV. The ion energy is referred to the maximum in the distribution with Eᵣ=5.7 eV. Symbols (closed and open circles and open triangles) indicate three different contributions. The horizontal bar indicates the possible range of peak position for each contribution.

FIG. 4. The peak positions of the three contributions shown in Fig. 3 are plotted as a function of the incident electron
energy, $E_i$. The broken straight lines indicate $E_{\text{a} \rightarrow \text{a}}$ given by Eq. (4). The $E_a$ values denote the possible $O^+O^-$ dissociation limits.

FIG. 5. Schematic potential-energy curves illustrating a dissociative attachment process accompanied with autodetachment. $E$ is the energy of the incident electron. $R_a$ is the turning point of potential curve $W^-(R)$ at the energy $E$, and $R_a$ is the crossing point of the two potential curves, $W^-(R)$ and $W(R)$.

FIG. 6. Schematic diagram illustrating the two effects: the shift of the $\sigma_{\text{DA}}(E)$ peak position relative to the $\sigma_{\text{AT}}(E)$ peak and the smaller $\sigma_{\text{DA}}(E)$ width in comparison with the $\sigma_{\text{AT}}(E)$ width.

FIG. 7. Semi-quantitative potential energy curves, which are based on the data in Table VII and the theoretical calculations of Refs. 32 and 33.
FIG. 1

O⁻ yield (Arbitrary units)

Electron energy (eV)

V_r =
-1.8 eV
-1.5 eV

O₂/W
O₂/Pt
O₂/Pt
O₂ (gas)
FIG. 2
FIG. 3
FIG. 4
Ground state

Potential energy

Internuclear distance

$O_2^-$ : $W^-(R)$

$O_2^* : W(R)$

$O + O$

$O + O^-$

$O_2$ Ground state

$R_E$

$R_C$

FIG. 5
$\text{FIG. 7}$
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>2</th>
<th>Dr. David Young</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 N. Quincy Street</td>
<td></td>
<td>Code 334</td>
<td></td>
</tr>
<tr>
<td>Arlington, Virginia 22217-5000</td>
<td></td>
<td>NORDA</td>
<td></td>
</tr>
<tr>
<td>Dr. Bernard Doula</td>
<td>1</td>
<td>Naval Weapons Center</td>
<td>1</td>
</tr>
<tr>
<td>Naval Weapons Support Center</td>
<td></td>
<td>Attn: Dr. Ron Atkins</td>
<td></td>
</tr>
<tr>
<td>Code 55C</td>
<td></td>
<td>Chemistry Division</td>
<td></td>
</tr>
<tr>
<td>Crane, Indiana 47522-5050</td>
<td></td>
<td>China Lake, California 93555</td>
<td></td>
</tr>
<tr>
<td>Naval Civil Engineering Laboratory</td>
<td>1</td>
<td>Scientific Advisor</td>
<td></td>
</tr>
<tr>
<td>Attn: Dr. R. W. Drisko, Code LSE</td>
<td></td>
<td>Commandant of the Marine Corps</td>
<td></td>
</tr>
<tr>
<td>Port Hueneme, California 93401</td>
<td></td>
<td>Code RD-1</td>
<td></td>
</tr>
<tr>
<td>Defense Technical Information Center</td>
<td>12</td>
<td>U.S. Army Research Office</td>
<td>1</td>
</tr>
<tr>
<td>Building S, Cameron Station, Alexandria, Virginia 22314</td>
<td>high quality</td>
<td>Attn: CDD-AI-IP</td>
<td></td>
</tr>
<tr>
<td>DTNSRDC</td>
<td></td>
<td>P.O. Box 12211</td>
<td></td>
</tr>
<tr>
<td>Attn: Dr. H. Singerman</td>
<td>1</td>
<td>Research Triangle Park, NC 27709</td>
<td></td>
</tr>
<tr>
<td>Applied Chemistry Division</td>
<td></td>
<td>Mr. John Boyle</td>
<td>1</td>
</tr>
<tr>
<td>Annapolis, Maryland 21401</td>
<td></td>
<td>Naval Ship Engineering Center</td>
<td></td>
</tr>
<tr>
<td>Dr. William Tolles</td>
<td>1</td>
<td>Philadelphia, Pennsylvania 19112</td>
<td></td>
</tr>
<tr>
<td>Superintendent</td>
<td></td>
<td>Naval Ocean Systems Center</td>
<td>1</td>
</tr>
<tr>
<td>Applied Chemistry Division, Code 6100</td>
<td></td>
<td>Attn: Dr. S. Yamamoto</td>
<td></td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td></td>
<td>Marine Sciences Division</td>
<td></td>
</tr>
<tr>
<td>Washington, D.C. 20375-5000</td>
<td></td>
<td>San Diego, California 91232</td>
<td></td>
</tr>
</tbody>
</table>
Dr. J. E. Jensen
Hughes Research Laboratory
3011 Malibu Canyon Road - Malibu, California 90265

Dr. J. H. Weaver
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. A. Reisman
Microelectronics Center of North Carolina Research Triangle Park, North Carolina 27709

Dr. M. Grunze
Laboratory for Surface Science and Technology
University of Maine
Orono, Maine 04469

Dr. J. Butler
Naval Research Laboratory
Code 6115
Washington D.C. 20375-5000

Dr. L. Interante
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Irvin Heard
Chemistry and Physics Department
Lincoln University
Lincoln University, Pennsylvania 19352

Dr. K. J. Klaubunde
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

Dr. C. B. Harris
Department of Chemistry
University of California
Berkeley, California 94720

Dr. R. Bruce King
Department of Chemistry
University of Georgia
Athens, Georgia 30602

Dr. R. Reeves
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Steven M. George
Stanford University
Department of Chemistry
Stanford, CA 94305

Dr. Mark Johnson
Yale University
Department of Chemistry
New Haven, CT 06511-8118

Dr. W. Kaufer
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, California 90265

Dr. Theodore E. Madey
Surface Chemistry Section
Department of Commerce
National Bureau of Standards
Washington, D.C. 20234

Dr. J. E. Demuth
IBM Corporation
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. M. G. Lagally
Department of Metallurgical and Mining Engineering
University of Wisconsin
Madison, Wisconsin 53706

Dr. R. P. Van Duyne
Chemistry Department
Northwestern University
Evanston, Illinois 60637

Dr. J. M. White
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Richard J. Saykally
Department of Chemistry
University of California
Berkeley, California 94720
ABSTRACTS DISTRIBUTION LIST, 056/629/629

Dr. G. A. Somorjai
Department of Chemistry
University of California
Berkeley, California 94720

Dr. J. Murday
Naval Research Laboratory
Code 6170
Washington, D.C. 20375-5000

Dr. W. T. Peirs
Electrical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Keith H. Johnson
Department of Metallurgy and
Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. S. Sibener
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Arold Green
Quantum Surface Dynamics Branch
Code 3817
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. S. L. Bernasek
Department of Chemistry
Princeton University
Princeton, New Jersey 08544

Dr. W. Kohn
Department of Physics
University of California, San Diego
La Jolla, California 92037

Dr. Stephen D. Kevan
Physics Department
University of Oregon
Eugene, Oregon 97403

Dr. David M. Walba
Department of Chemistry
University of Colorado
Boulder, CO 80309-0215

Dr. L. Kesmodel
Department of Physics
Indiana University
Bloomington, Indiana 47403

Dr. K. C. Janda
University of Pittsburgh
Chemistry Building
Pittsburgh, PA 15260

Dr. E. A. Irene
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 SNH
UNITED KINGDOM

Dr. H. Tachikawa
Chemistry Department
Jackson State University
Jackson, Mississippi 39217

Dr. John W. Wilkins
Cornell University
Laboratory of Atomic and
Solid State Physics
Ithaca, New York 14853

Dr. Ronald Lee
R301
Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910

Dr. Robert Sommer
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Noria Metiu
Chemistry Department
University of California
Santa Barbara, California 93106

Dr. W. Goddard
Department of Chemistry and Chemical
Engineering
California Institute of Technology
Pasadena, California 91125
<table>
<thead>
<tr>
<th>Name</th>
<th>Institution and Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. John T. Yates</td>
<td>Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260</td>
</tr>
<tr>
<td>Dr. F. Carter</td>
<td>Naval Research Laboratory, Washington, D.C. 20375-5000</td>
</tr>
<tr>
<td>Dr. Richard Colton</td>
<td>Naval Research Laboratory, Washington, D.C. 20375-5000</td>
</tr>
<tr>
<td>Dr. Dan Pierce</td>
<td>National Bureau of Standards, Optical Physics Division, Washington, D.C. 20234</td>
</tr>
<tr>
<td>Dr. R. G. Wallis</td>
<td>Department of Physics, University of California, Irvine, California 92664</td>
</tr>
<tr>
<td>Dr. D. Basler</td>
<td>Chemistry Department, George Washington University, Washington, D.C. 20052</td>
</tr>
<tr>
<td>Dr. J. C. Hemminger</td>
<td>Chemistry Department, University of California, Irvine, California 92717</td>
</tr>
<tr>
<td>Dr. T. F. George</td>
<td>Chemistry Department, University of Rochester, New York 14627</td>
</tr>
<tr>
<td>Dr. G. Rubloff</td>
<td>IBM, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598</td>
</tr>
<tr>
<td>Dr. J. Baldeschwiezer</td>
<td>Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125</td>
</tr>
<tr>
<td>Dr. Galen D. Stucky</td>
<td>Chemistry Department, University of California, Santa Barbara, CA 93106</td>
</tr>
<tr>
<td>Dr. A. Steck</td>
<td>Department of Electrical and Systems Engineering, Rensselaer Polytechnic Institute, Troy, New York 12181</td>
</tr>
<tr>
<td>Dr. R. P. Messmer</td>
<td>Materials Characterization Lab, General Electric Company, Schenectady, New York 22217</td>
</tr>
<tr>
<td>Dr. J. T. Keiser</td>
<td>Department of Chemistry, University of Richmond, Richmond, Virginia 23173</td>
</tr>
<tr>
<td>Dr. R. W. Plummer</td>
<td>Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104</td>
</tr>
<tr>
<td>Dr. E. Yeager</td>
<td>Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106</td>
</tr>
<tr>
<td>Dr. N. Winograd</td>
<td>Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802</td>
</tr>
<tr>
<td>Dr. Roald Hoffmann</td>
<td>Department of Chemistry, Cornell University, Ithaca, New York 14853</td>
</tr>
<tr>
<td>Dr. Robert L. Whetten</td>
<td>Department of Chemistry, University of California, Los Angeles, CA 90024</td>
</tr>
<tr>
<td>Dr. Daniel M. Neumark</td>
<td>Department of Chemistry, University of California, Berkeley, CA 94720</td>
</tr>
<tr>
<td>Dr. G. H. Morrison</td>
<td>Department of Chemistry, Cornell University, Ithaca, New York 14853</td>
</tr>
</tbody>
</table>