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Kinetic-energy distributions of O^- produced by dissociative electron attachment to O_2 physisorbed on a Kr substrate

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We report measurements of the kinetic-energy (E_k) distributions of O^- produced by low-energy electron impact (6–18 eV) on thin disordered films consisting of 0.15 ML of O_2 physisorbed on 5 ML of Kr, all condensed on polycrystalline Pt. The present measurements confirm that, for incident electron energies $E(e) \leq 12$ eV, dissociative electron attachment (DEA) to physisorbed O_2 involves the $^2\Pi_u$, $^2\Sigma_u^+$ (I), and $^2\Sigma_g^+$ (I) resonances of O_2^{-*}; of these, only the latter is found to dissociate to the *second limit* $O^-(^2P)+O(^1D)$, via a nonadiabatic curve crossing. Above $E(e)=12$ eV, DEA to O_2 is found to proceed mainly via the $^2\Sigma_x^+$ (II) [$x=g$ and/or u] state(s), leading to $O^-+O(^1D)$ fragments. No evidence for O_2^{-*} resonance states which dissociate to the *third limit* $O^-+O(^1S)$ is found below $E(e)=18$ eV. The results also support the general notion that postdissociation interactions which lead to ion energy loss consist mainly of binary large-angle elastic collisions of the desorbing O^- with adsorbate particles in the van der Waals solid. Contributions of energy-loss electrons to the DEA O^- E_k distributions are found to most likely originate in small O_2 clusters at, or near, the surface of the Kr substrate.

I. INTRODUCTION

Low-energy (0–20 eV) electron interactions with physisorbed O_2 molecules may lead to the production of O^- fragments via two processes: (a) dissociative electron attachment (DEA)

$$e^- + O_2(^3\Sigma_g^-) \rightarrow O_2^{-*} \rightarrow O^- + O(^3P \text{ or } ^1D) ,$$

and (b) dipolar dissociation (DD)

$$e^- + O_2(^3\Sigma_g^-) \rightarrow O_2^* + e^- \rightarrow O^- + O^+ + e^- .$$

Of these, *only* DEA involves the formation of temporary molecular anion resonances, the symmetries and dissociation limits of which partially determine the final internal state of the neutral fragment, as well as the kinetic energies (E_k) of the dissociating products. The threshold for DD is near 17 eV, or about 12.5 eV above the threshold for DEA. In a recent paper[1] (henceforth referred to as I) we presented measurements of electron-stimulated desorption (ESD) O^- E_k distributions, as well as high-resolution electron energy-loss (HREEL) spectra, from pure O_2 multilayer solids. In that study, we proposed that in addition to the previously invoked O_2^{-*} resonances ($^2\Pi_u$, $^2\Sigma_g^+$(I), and $^2\Sigma^+$(II){g and/or u}), DEA may also involve the $^2\Sigma_u^+$(I) state, which had formerly been assumed to be too short lived to result in observable O^- yield.[2] Unlike the $^2\Sigma_g^+$(I) state, which dissociates predominantly into the *second limit* $O^-+O(^1D)$ via a nonadiabatic curve crossing,[2,3] the $^2\Sigma_u^+$(I) state is believed to dissociate into the *first limit* $O^-+O(^3P)$. Generally, for isolated, i.e., gas phase, ground-state $O_2(^3\Sigma_g^-)$, transitions to $O_2^{-*}(\Sigma^+)$ states are forbidden by symmetry selection rules; however, based on the large amount of evidence from condensed phase O_2 (e.g., Refs. 4–7), and CO,[8] cluster (e.g., Refs. 9–13), as well as state-specific gas phase $e^-+O_2(^1\Delta_g)$ experiments,[3] it is generally believed that in the condensed phase this $\Sigma^- \nleftrightarrow \Sigma^+$ selection rule is relaxed due to the breaking of the cylindrical symmetry of the molecular wave function by adjacent molecules. Therefore, the difference between the gas and condensed phase O^- yield (or cross section), shown in Figs. 1(a) and 1(b), has been attributed mainly to the occurrence of

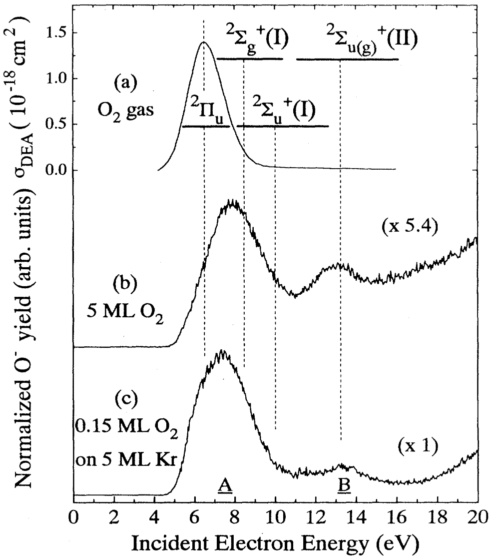

FIG. 1. (a) Total cross sections for DEA to O_2, measured in the gas phase (Ref. 31); also shown are O^- yields per unit O_2 concentration, obtained in the present experiments from low-energy electron impact on (b) 5 ML of O_2, and (c) 0.15-ML O_2 on 5-ML Kr (all condensed on polycrystalline Pt), as functions of incident electron energy. The dashed vertical and thick horizontal lines, respectively, indicate the approximate positions and extent of the anion resonances in the Franck-Condon region, as discussed in the text. The multiplicative factor of 5.4 is that required to normalize the peak height of the largest peak (region A) in (b) to that in (c).

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DEA via the Σ^+ states of $O_2{}^{-*}$.

In I we also demonstrated that several particular condensed phase mechanisms may not only influence the yield, but also the E_k distributions of the desorbing anions. They are (i) electron energy loss (EEL) mainly to electronic excitations of O_2 molecules in the solid prior to DEA, (ii) postdissociation interactions (PDI), such as binary large-angle elastic collisions, of the anion fragment with molecules at the surface, or in the bulk, of the solid, and (iii) the effects of the charge-induced polarization energy (E_p) of the solid on both the temporary $O_2{}^{-*}$ resonance and the desorbing anion fragment. EEL and PDI in particular tend to broaden the $O^- E_k$ distributions, which in turn may "smear out" the individual contributions of certain overlapping $O_2{}^{-*}$ states, with different dissociation limits, to a given O^- E_k distribution [e.g., the ${}^2\Sigma_g^+$(I) and ${}^2\Sigma_u^+$(I) resonances for $E(e)\approx 9$ eV].

We therefore suggested in I that the effects of EEL and PDI on the O^- E_k distributions could perhaps be reduced by physisorbing small amounts of O_2 on a rare-gas substrate. Solid Kr, for example, has an E_p similar to that of solid O_2,[14] yet no exciton formation below about 9.8 eV (Ref. 15) (thus reducing EEL in the substrate below that energy), and the constituent Kr atoms have larger mass than O_2 (thus reducing momentum transfer in elastic collisions prior to desorption). Therefore, in this paper we present ESD O^- E_k distributions obtained from condensed solids consisting of 0.15 ML of O_2 physisorbed on 5 ML of Kr. The incident electron energy scale ranges from 6 to 18 eV, for which a typical anion yield function is shown in Fig. 1(c). By comparing the results to those obtained from pure O_2 multilayer solids, we hope to show that it is possible to identify individual contributions of certain $O_2{}^{-*}$ resonances to the E_k distributions, *particularly* those of the ${}^2\Sigma_u^+$(I) state. We will also demonstrate that the present results are compatible with the notion that anion collisions in the solid consist mainly of binary large angle elastic scattering events (single and/or multiple), and that the remaining contributions of EEL to the measured E_k distributions are likely to originate in small O_2 clusters at the surface of the Kr substrate.

II. EXPERIMENTAL METHOD

The ESD apparatus (including the sample geometry and ion optics) and experimental methods used in the present investigation have been described in great detail in I and elsewhere.[16] Only a brief description is given below.

The experiments are performed in a UHV chamber at a base pressure of 10^{-10} Torr. The entire experimental assembly is enveloped by a double Mu-metal shield, which reduces the residual magnetic field in the experimental volume to less than 15 mGauss.

The O_2 sample gas is condensed directly onto a multilayer substrate film which covers a 0.00075-cm-thick polycrystalline Pt foil. This foil is press fitted directly onto the cold tip (17 K) of a closed cycle cryostat, and is cleaned by resistive heating. The substrate film is prepared by condensing 5 ML of Kr gas onto the surface of the Pt foil. The film thickness is determined by means of a volumetric dosing procedure[17] with an estimated uncertainty of 50%, and a reproducibility of ±0.02 ML. The fractional coverage of O_2 is 0.15 ML deposited on 5 ML of Kr, whereas for the pure oxygen films 5 ML of O_2 are condensed directly onto the Pt foil. The purities of the sample gases are 99.998% for O_2, and 99.995% for Kr. Since it is known that the ESD O^- yields may change slightly over time due to O_2 diffusion through the Kr film,[18] each measurement is obtained immediately after the O_2 is deposited onto a Kr substrate. This also minimizes the contamination of the surface by any residual background gases.

A hemispherical electron monochromator produces an electron beam with a resolution of 80 meV full width at half maximum (FWHM) intensity, and a spatial diameter, at the target, of 0.2 cm. The absolute energy scale of the incident electron beam is determined to within ±0.15 eV of the vacuum level (here $E_{\text{vac}} \equiv 0.0$ eV) by observing the onset of current transmission to the Pt foil as a function of incident electron energy $E(e)$. Energy shifts of this onset determine the amount of charging of the condensed films.[19] It is therefore possible to verify that all experimental results are obtained under essentially charge-free conditions. The electron beam intensity, measured at the target, is at most 1.0 nA for $1.0 \le E(e) \le 20$ eV.

The monoenergetic electron beam strikes the target film at an angle of 70° with respect to the surface normal $\hat{\mathbf{u}}$, where it may promote anion formation via DEA and DD. Some of the negative-ion fragments possess sufficient E_k to overcome the E_p at the surface of the solid and emerge into the vacuum. A fraction of these anions enter a quadrupole mass spectrometer (QMS), which is positioned at 20° from $\hat{\mathbf{u}}$, and are detected by a standard pulse counting channel electron multiplier. The ion optics, preceding the QMS, contains a set of grids; by applying a certain voltage to these grids, anions of particular energies may be prevented (i.e., retarded) from entering the QMS. Transmission characteristics of the ion optics, grids, and QMS have been discussed in I. Briefly, for O^- with *in vacuo* E_k between 0.1 and 4 eV, the average transmission is estimated to be about 32%. For the same range of anion energies, the experimentally observable range of desorption angles (ϕ), of those O^- transmitted through the ion optics, is about $1° \le \phi \le 45°$ with respect to $\hat{\mathbf{u}}$.

The ESD apparatus may be used in two modes: (a) In the *ion yield mode* the QMS is set to transmit only O^-, and the retardation voltage on the grids is set to pass anions of all energies. When $E(e)$ is varied between 0 and 20 eV, an ion yield curve is obtained (see Fig. 1). (b) In the *ion energy mode*, both the $E(e)$ and mass selection of the QMS remain fixed, and the O^- signal intensity is monitored as the retardation voltage is scanned over a suitable range. An E_k distribution is obtained by numerical differentiation of the smoothed retardation curve. The peak of the E_k distribution, which is usually of a Gaussian shape, defines the *most probable kinetic energy* [E_k(mp)], and the FWHM of the entire distribution defines the width ($W_{1/2}$). When several structures are present in an E_k distribution, a multiple Gaussian fit is used to obtain the respective peak positions, i.e., E_k(mp). As discussed in detail in I, the *maximum observable kinetic energy* [E_k(max)] is defined directly from the measured retardation curves as that retardation voltage for which the O$^-$ intensity is reduced down to 1% of the unretarded signal.

Measurements of the above parameters, as well as the shapes of the E_k distributions, are repeatable to well within 10%. All the contributions to the experimental uncertainties, indicated by error bars throughout this paper, have been discussed extensively in I, they are comprised mainly of contact potentials which contribute an absolute uncertainty of about ±0.25 eV to both the E_k(mp) and E_k(max).

III. RESULTS AND DISCUSSION

For the discussion of the experimental results we make three assumptions with respect to the character of the condensed multilayer films and their surface. (1) For the present fixed substrate thicknesses, the effects of the Pt metal on the DEA process are known to be small.[20] (2) As discussed recently,[21] the Kr substrate, when prepared far below its sublimation temperature, is found to be sufficiently disordered such that the O_2 molecules are expected to physisorb onto it with more or less random orientations. Thus, given this sort of film and the ion optics' large range of observable desorption angles, effects of substrate ordering and preferential O_2 adsorption angles[22] are considered to be negligible, and are excluded from the subsequent discussion. (3) It has also been demonstrated

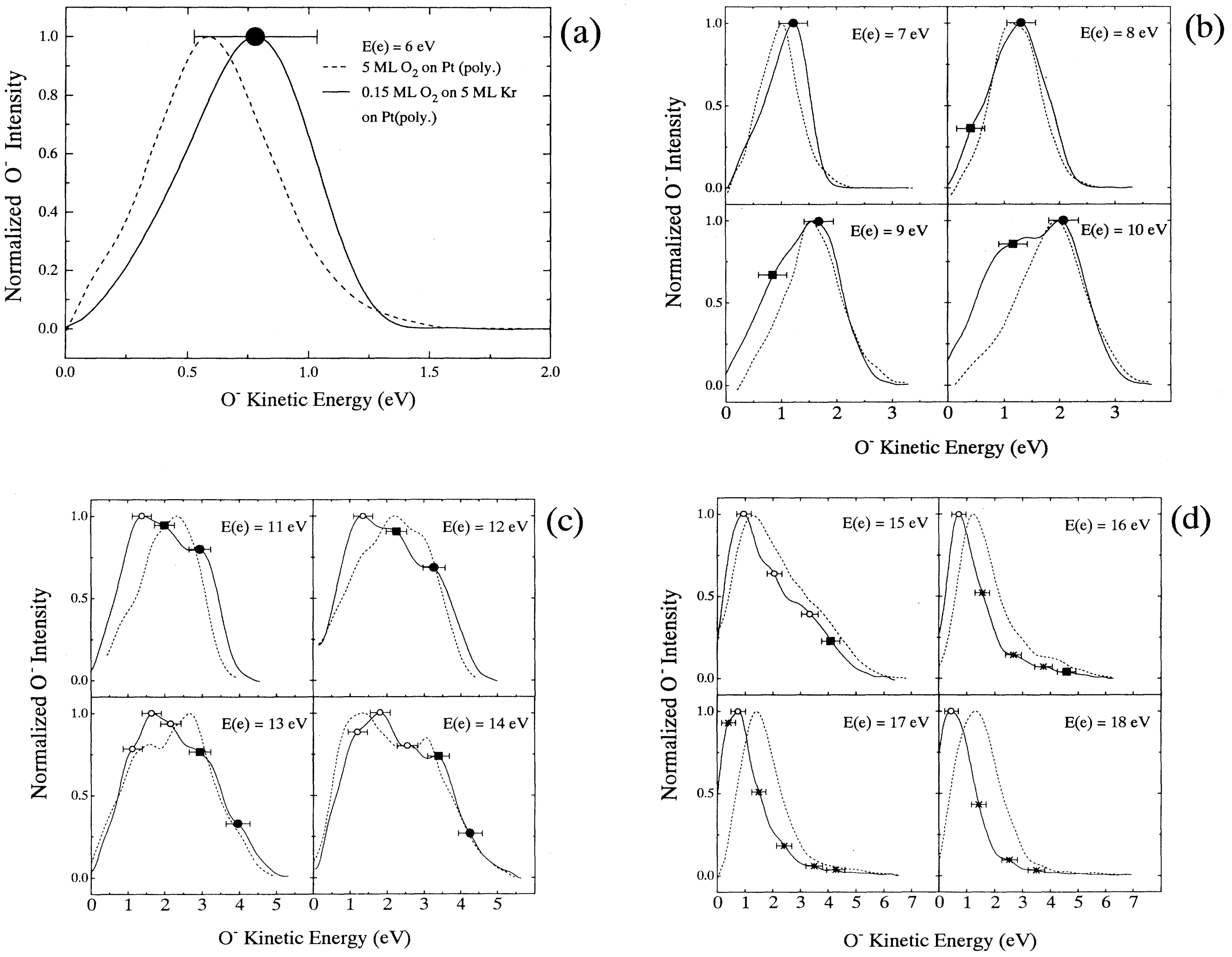

FIG. 2. (a)–(d) O$^-$ E_k distributions obtained in the present experiments from 0.15-ML O_2 on 5-ML Kr (solid curves), and 5-ML O_2 (dashed curves), all condensed on polycrystalline Pt, for incident electron energies, $E(e)$, between 6 and 18 eV. The solid circles and squares indicate features attributed to dissociative electron attachment (DEA) induced by unscattered and/or (quasi) elastically scattered electrons, whereas the open circles, for $E(e) < 17$ eV, and all stars indicate DEA by electrons that have lost significant amounts of energy in the solid prior to attachment.

that the condensed phase O_2 DEA cross section is greatly enhanced relative to the gas phase, e.g., by about a factor of 20 for DEA via the $^2\Pi_u$ state of O_2^{-*} on a Kr substrate.[23] This enhancement is believed to be the result of a lowering of the O_2^{-*} potentials, relative to the neutral ground state, by the E_p of the solid film. The E_p for solid O_2 is estimated to be about 0.7 eV,[14] whereas that for solid Kr is similar at about 0.72 eV.[14] Thus, in the present context, we may assume (with caution[24]) that the condensed phase enhancement of the DEA cross section is sufficiently similar for the O_2 and Kr solids.

We finally note that the relaxation of the $\Sigma^- \not\leftrightarrow \Sigma^+$ selection rule for DEA to O_2 requires the presence of adjacent *molecules* such as O_2,[4] CO or N_2.[5] For reasons that are not yet understood, neighboring *rare-gas atoms do not appear to cause relaxation of the above selection rule.*[25] Since, at low O_2 coverage, the probability of finding two (or more) molecules adjacent to each other at the surface of a rare-gas solid is reduced,[14] so is the probability of formation of Σ^+ states of O_2^{-*}. Thus, we expect a reduction in the relative contribution of these states to the total anion signal [compare peak ratios B/A in Figs. 1(b) and 1(c)], as well as the E_k distributions.

Figures 2(a)–2(d) show the present measurements of the ESD O^- E_k distributions obtained from 0.15-ML O_2 physisorbed on a 5-ML Kr substrate (solid curves) for 6 eV$\leq E(e) \leq$18 eV. Also shown for comparison are O^- E_k distributions obtained concurrently, under identical experimental conditions, from 5-ML solids of pure O_2 (dashed curves). These latter measurements are in excellent agreement with those presented in I. Structures in the E_k distributions from the O_2-Kr films (solid curves) are indicated with various symbols. As we hope to show presently, they are the result of *direct* DEA via O_2^{-*} resonances which dissociate to the *first* (solid circles) and *second* (solid squares) *limits,* respectively, induced by unscattered and/or (quasi-) elastically scattered electrons. The open circles for $E(e) \leq 16$ eV, and all stars indicate *indirect* DEA by electrons that have lost significant amounts of energy prior to attachment.

A. DEA by unscattered and/or (quasi)elastically scattered electrons

We had shown in I that in the condensed phase the *in vacuo* $E_k(O^-)$, i.e., the E_k of the anion *after* desorption, may be generally written as

$$E_k(O^-) = \tfrac{1}{2}\{E(e) - [D_0 - A_e] - E^*\} - \left\{ \frac{\Delta E(e) + E_p}{2} + \Delta E(O^-) \right\} . \quad (1)$$

Here, $E(e)$ is the incident electron energy, D_0 the dissociation energy of O_2 [about 5.08 eV (Ref. 26)], and A_e the electron affinity of O [1.46 eV (Ref. 27)]. E^* is the internal energy of the *neutral* DEA fragment, i.e., it equals 0 eV for dissociation to the *first limit* $O^- + O(^3P)$, and about 2 and 4.2 eV for dissociation to the *second* and *third limits* $O^- + O(^1D)$ and $O^- + O(^1S)$, respectively. The condensed state effects are contained in the second term, where the magnitudes of EEL, ion energy loss PDI, and the solid's average polarization energy are designated, respectively, by $\Delta E(e)$, $\Delta E(O^-)$, and E_p.[28]

As shown in I, the effect of the second term on the *most probable* kinetic energy, E_k(mp), was observed to be relatively small. It was found to lower the E_k(mp), for certain ranges of electron energies, by about 0.77 eV on the average, viz.,

$$E_k(\mathrm{mp}) = \tfrac{1}{2}\{E(e) - [D_0 - A_e] - E^*\} - \{0.77 \text{ eV}\} . \quad (2)$$

The net contribution of the E_p to the 0.77-eV term amounts to about 0.36 eV ($= E_p/2$), which will be similar for pure O_2 and O_2-Kr solids, due to their similar E_p. The remainder is attributed to some small combined average contribution from quasielastic EEL (e.g., multiple phonon losses $\leq$0.3 to 0.35 eV (Ref. 29)] and/or ion energy loss PDI. Thus, all other things being equal for the O_2-Kr solid, we expect the electron energy dependence of those features in the E_k distributions, which are the result of *direct* DEA by unscattered, elastically and quasielastically scattered electrons, to follow either of the straight lines, of slope $\frac{1}{2}$, described by Eq. (2) for the three different dissociation limits. This can be seen in Fig. 3, which shows the different O^- E_k(mp) [i.e., the solid circles and squares, and open circles from Figs. 2(a)-2(d)] as functions of incident electron energy. The thick solid curves represent our previous results from pure O_2 multilayer solids as discussed in I, which are in good agreement with our present control experiments [dashed curves in Figs. 2(a)–2(d)]. The features designated by stars in the E_k distributions are not shown for clarity. Thus, from Figs. 3, and 2(a)–2(d), we conclude the following: (1) generally, the features marked by open circles and stars in the E_k distributions represent O^-

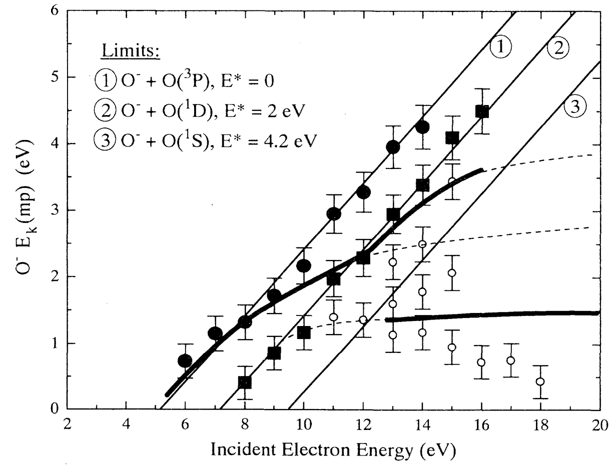

FIG. 3. O^- E_k(mp) (solid circles and squares, open circles) obtained from the E_k distributions in Figs. 2(a)–2(d), as functions of incident electron energy. The numbered straight lines of slope $\frac{1}{2}$ correspond to Eq. (2) for the three indicated dissociation limits. The thick solid curves represent our previous results from pure O_2 solids as discussed in I. The dashed lines are guides to the eye.

production via *indirect* DEA, induced predominantly by electrons which have experienced significant EEL prior to attachment. (2) Within the present experimental uncertainties, the features marked by solid circles and squares indicate that, for $E(e) \leq 16$ eV, unscattered and/or (quasi) elastically scattered electrons may induce *direct* DEA to physisorbed O_2 via molecular anion resonances that dissociate *exclusively* to the *first* and *second limits* [no systematic evidence is seen that indicates resonances that dissociate to the *third* limit $O^- + O(^1S)$]. Approximate intramolecular potentials for these O_2^{-*} states have already been presented in I; their shapes and positions in the Franck-Condon region of the neutral ground state $O_2(^3\Sigma_g^-)$ were based in part on the theoretical work of Sambe and Ramaker,[2] Michels,[30] as well as the previous experimental results discussed in I.

Within the context of these potential curves, DEA to physisorbed O_2 may be summarized by Fig. 3: for $E(e) < 8.5$ eV *direct* DEA proceeds, much like in the gas phase,[31] via formation of the $^2\Pi_u$ resonance of O_2^{-*}, which dissociates to the *first limit,* $O^- + O(^3P)$. For 8 eV $\leq E(e) \leq 12$ eV, unscattered and/or (quasi) elastically scattered electrons may *directly* induce O^- formation via either the $^2\Sigma_g^+$(I), or the $^2\Sigma_u^+$(I) resonance of O_2^{-*}, of these, the $^2\Sigma_u^+$(I) dissociates to $O^- + O(^3P)$, according to Wigner-Witmer selection rules.[32] The $^2\Sigma_g^+$(I) resonance, however, dissociates to the *second limit,* $O^- + O(^1D)$, via a nonadiabatic curve crossing (i.e., near degeneracy) with the $^2\Sigma_g^+$(II) state. This latter observation is in agreement with *ab initio* calculations,[30] as well as $e^- + O_2^*(a\,^1\Delta_g)$ DEA experiments in the gas phase.[3]

Additional evidence for the $^2\Sigma_u^+$(I) state may be seen in Fig. 4(a), which shows the maximum observed O^- E_k, i.e., E_k(max), as a function of $E(e)$. The E_k(max) corresponds to that very small fraction of O^- (i.e., about 1% of the signal) that desorbs into the vacuum following negligible inelastic processes, and under reduced effects of the E_p; consequently, the two straight lines representing the two dissociation limits are obtained by only the first term in Eq. (1). Figure 4(a) indicates that (in addition to the $^2\Pi_u$ state) for $E(e)$ less than about 13 or 14 eV, there exists always a negative-ion resonance that dissociates to the *first limit,* i.e., the $^2\Sigma_u^+$(I). The latter is supported by the observation that the O^- E_k(max) extracted from the measurements of Azria *et al.* (open circles[33]) for pure O_2 solids show good agreement with the present measurements.[34] We thus find that the present results strongly confirm our suggestion presented in I, namely, that DEA to physisorbed O_2 *must* involve formation of the $^2\Sigma_u^+$(I) resonance; this O_2^{-*} state had previously been speculated[2] to be too short lived to result in observable O^- signal, based exclusively on the observation that its molecular orbital configuration is similar to that of the $^4\Sigma_u^-$ state, which itself is actually known to possess a very short lifetime towards autodetachment.[35,36]

We note that, although for $E(e) > 13$ eV, the solid circles in Fig. 3 do suggest dissociation to the *first limit,* i.e., presumably still via the $^2\Sigma_u^+$(I) state, this interpretation is complicated by the fact that here the nonadiabatic curve crossing between the two Σ_g^+ states may, at least in principle, imply some contribution from dissociation of the $^2\Sigma_g^+$(II) resonance into the *first limit.*

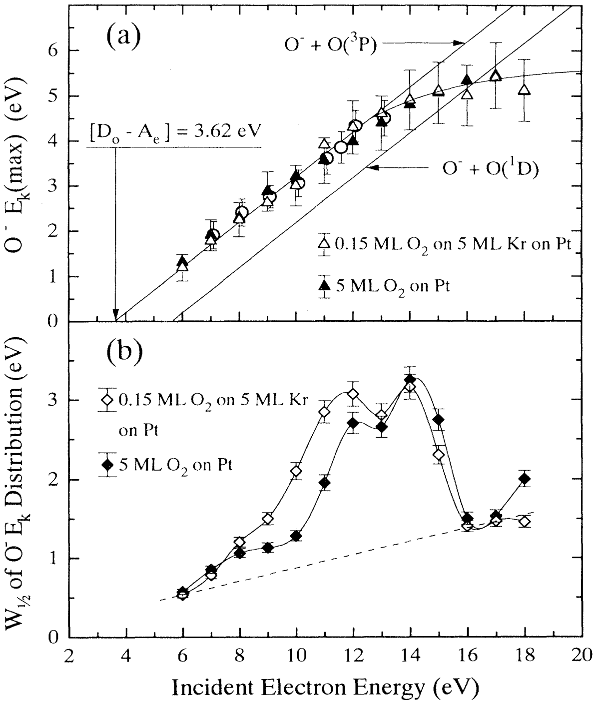

FIG. 4. (a) E_k(max) and (b) $W_{1/2}$, of the O^- E_k distributions, shown in Fig. 2(a)–2(d), as functions of incident electron energy. The triangles and diamonds represent the present results, whereas the open circles in (a) depict the O^- E_k(max) extracted from the measurements of Ref. 6 on pure O_2 films. In (a), the straight solid lines of slope $\frac{1}{2}$, indicating the two dissociation limits, correspond to the first term in Eq. (1), whereas in (b) the straight dashed line represents the estimate of the background contribution to the $W_{1/2}$, as discussed in I. In both (a) and (b) the thin curves through the data are guides to the eye.

Finally, for about $E(e) > 12$ eV, the solid squares may unfortunately not be attributed to an O_2^{-*} resonance with a *known g/u* symmetry. As discussed explicitly in I, we may only conclude with certainty that at these $E(e)$, DEA also proceeds via formation of a gas-phase-forbidden molecular anion resonance that dissociates to the *second limit,* i.e., the $^2\Sigma^+$(II) state(s) with g and/or u symmetry. The reason for this lies chiefly with the substantially different theoretical estimates for the position of the $^2\Sigma_u^+$(II) resonance in the Franck-Condon region of the ground-state $O_2(^3\Sigma_g^- v=0)$.

B. EEL and PDI effects on the ESD of O$^-$

From Eq. (1) it can be seen that, for a fixed incident $E(e)$, a given E_k distribution may contain contributions from direct and various indirect processes. Our HREEL spectra reported in I, as well as previous measurements[36] demonstrated that for pure O_2 solids the EEL effects [i.e., the magnitude of $\Delta E(e)$] on the E_k distributions become only significant at higher incident electron energies: for $E(e)$ less than approximately 9.5 to 10 eV, at most 30%

of the incident electrons will lose $\Delta E(e)>0.3$ eV. For higher $E(e)$, at least 50% of the incident electrons experience EEL events; of these, 72% to 90% consist of Schumann-Runge [$\Delta E(e)>7$ eV] and ACc [4.2 eV $<\Delta E(e)<7$ eV] excitations.[37] Thus, for $E(e)>10$ eV, it was demonstrated in I that the additional (low-energy), broad structure in the O^- E_k distributions from pure O_2 solids is mainly the result of EEL prior to DEA.

Since the lowest exciton energy of Kr lies near 9.8 eV, we find in the present experiments that, for 10 eV $<E(e)<15$ eV, the broad feature marked by the open circles in Fig. 2(c) is predominantly the result of EEL due to electronic excitations of *oxygen molecules.* However, for $E(e)\geq 15$ eV, electrons that lose energy to excitations in the Kr substrate will have sufficient energy to induce DEA to O_2; this may in part explain the reduction in $W_{1/2}$ and lower peak position of the E_k distributions, for $E(e)\geq 16$ eV [Fig. 2(d)], relative to the pure O_2 solid. It is of interest to note that despite the much lower O_2 concentration for the O_2-Kr solid, the E_k distributions contain such large quantities of O^- produced by electrons that have experienced significant EEL to $O_2{}^*$ excitations prior to DEA. In fact for 11 eV $\leq E(e)\leq 14$ eV, about 30 % to 60% of the O^- appear to be the result of this process. At the same time we find that the remaining 70% to 40% of the DEA O^- are produced by unscattered and/or (quasi) elastically scattered electrons exclusively via gas-phase-forbidden transitions to Σ^+(I and II) resonance states of $O_2{}^{-*}$. Since DEA via these Σ^+ states requires the presence of at least two adjacent O_2 molecules, the latter observation implies that the amount of O_2 surface clustering on the Kr substrate is much larger than the 5% maximum predicted by a simple statistical model.[38] This in turn is expected to increase the average distance between O^- production sites, which suggests that EEL followed by DEA is more likely to occur within the same cluster.

As seen in Figs. 4(b) and 2(b), for 8 eV $<E(e)<11$ eV, the $W_{1/2}$ of the O^- E_k distributions from the O_2-Kr solids are significantly broadened towards lower anion energies, relative to those from the pure O_2 solid. This increased desorption signal of low-energy O^- from a Kr substrate is consistent with the notion put forth in I that those PDI that lead to a reduction in O^- E_k consist mainly of binary large-angle elastic collisions with adjacent particles in the physisorbed van der Waals solid: for an elastic O^-+M collision, momentum transfer is significantly larger for $M=O_2$ than for M = Kr; thus, from a classical hard-sphere scattering approximation[39] we find that, for projectile scattering angles (in the laboratory frame) from 5° to 180°, the $\Delta E(O^-)$ for a Kr target is 60% to 40% less than for an O_2 target. For these elastic collisions the scattering angle (i.e., the magnitude of momentum transfer) is always large for small impact parameters b, which is the case here where the maximum b is at most half of the solid's lattice spacing. Depending on the particular adsorption angles of the O_2 at the surfaces of the disordered solids, a given number of O^- fragments will scatter through comparable angles, regardless of the substrate. Thus, those DEA O^- that are already formed with low E_k, e.g., those from dissociation of the $^2\Sigma_g^+$(I) state, are less likely to possess sufficient $E_k>E_p$ if they scatter in an O_2, rather than a Kr substrate [see Fig. 2(b)]. In support of the above discussion we note that very recent experiments[40,41] on the transmission of low-energy O^+ ($E_k\approx 7$ eV) through thin films of Ar, Kr, and Xe, and F^- (F^+) ($E_k\approx 5$ eV) through PF_3, H_2O, and rare-gas layers, clearly underscore the importance of large-angle elastic scattering in the ion desorption dynamics.[42]

The above considerations on elastic scattering PDI may also explain why, for $E(e)\geq 17$ eV [see Fig. 2(d)], where DD becomes possible, the peak position of the O^- E_k distribution from the O_2-Kr solid is so much lower than that from the pure O_2 film (i.e., why there are more low-energy O^- able to desorb from the Kr solid): the O^- E_k distributions for $E(e)=17$ and 18 eV are expected to contain anion fragments formed by DD with E_k barely sufficient to overcome the E_p of the solid. Thus, those DD O^- that scatter elastically in an O_2 substrate will generally no longer be able to desorb, whereas a large proportion of the DD O^- scattered from a Kr substrate will.

IV. SUMMARY AND CONCLUSIONS

We have presented measurements of O^- E_k distributions obtained from disordered solids consisting of 0.15 ML of O_2 physisorbed on 5 ML of Kr, all condensed on polycrystalline Pt. Our measurements demonstrate that on a rare-gas substrate the contributions of various DEA $O_2{}^{-*}$ resonance states to the E_k distributions may be more clearly resolved, relative to comparable measurements from pure O_2 multilayer solids. This is attributed mainly to a reduction of large-angle elastic scattering PDI of the DEA O^- in the Kr substrates. We also find that the remaining EEL contributions to the O^- E_k distributions most likely originate within small surface clusters of O_2 at the surface of the Kr solid; it is estimated that as much as two-thirds of the O_2 may physisorb on the Kr substrate in groups of two or more molecules.

It is the main conclusion of this paper that, for $E(e)<20$ eV, DEA to physisorbed ground-state O_2 ($^3\Sigma_g^- v=0$) may involve *all* of the $O_2{}^{-*}$ resonance states proposed in I, in particular the $^2\Sigma_u^+$(I) state near 10 eV. Unfortunately, the g/u symmetry of the $^2\Sigma^+$(II) state(s) involved in DEA, cannot be determined experimentally at this time; we therefore suggest that more theoretical work be undertaken to remove this remaining ambiguity.

The motivation for the continuing work on DEA to condensed molecules lies in its wide range of applications, which extend from radiobiology,[43] to the prediction of aging and dielectric breakdown characteristics of insulating materials.[44] Also, as noted in I, the prospect of *tunable surface chemistry*, i.e., the *in situ* modification of surfaces by ionic (or neutral) radicals, requires an understanding of the basic processes by which the interacting components, e.g., DEA fragments, are produced at these surfaces.

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[24] The downshift of the $O_2{}^{-*}$ potential, by an amount equal to E_p, effectively reduces the internuclear bond length, R_c, beyond which autodetachment is no longer possible; this increases the survival probability of the dissociating $\{O^- + O\}$ complex, and hence the DEA cross section. However, since the survival probability depends exponentially on R_c, a small change in E_p (and hence in R_c) may significantly affect the magnitude of this cross-section enhancement.

[25] See Ref. 14. This effect is most predominant for O_2 on Ar [see H. Sambe, D. E. Ramaker, L. Parenteau, and L. Sanche, Phys. Rev. Lett. **59**, 505 (1987)], where it is found that for O_2 concentrations well below 0.1 ML, the electron energy dependence of the O^- ESD yield below 16 eV is virtually identical to that found in the gas phase, where DEA to ground-state molecules is allowed *only* via the $^2\Pi_u$ resonance.

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[28] Note that the first term represents the *intrinsic* energetics of the DEA reaction, i.e., that minimal thermodynamic relationship which must always apply. The condensed state effects, any combination of which may occur (and which depend in part on the location of the O_2), therefore determine the final E_k of a *desorbed* anion.

[29] EEL due to multiphonon excitations are generally similar, at about ≤ 0.3 to 0.35 eV, for multilayer solids consisting of either physisorbed Ar, Kr, and Xe [M. Michaud, P. Cloutier, and L. Sanche, Phys. Rev. B **44**, 10 485 (1991)], or N_2 [M. Michaud, P. Cloutier, and L. Sanche, Phys. Rev. B **49**, 8360 (1994)], as well as physisorbed CO and O_2 [M. Michaud, P. Cloutier, and L. Sanche (unpublished)].

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[34] Figure 4(a) also seems to suggest that, regardless of the character of the solid (e.g., the present disordered multilayers of pure O_2 and O_2/Kr, or the somewhat more ordered films of Ref. 6), there is always a very small number of physisorbed O_2 *(at most 1%)* for which the combined effects of not only EEL and PDI, but also E_p are minimized, at least within the limits of our experimental uncertainties. For these few molecules, DEA results in fragments with E_k equal, or *very nearly* equal, to those obtained from the first term in Eq. (1). These molecules, however, still seem to be subject to the relaxation of the $\Sigma^- \not\leftrightarrow \Sigma^+$ selection rule, which requires only *one* nearest neighbor (which in itself would greatly reduce the effects of E_p, and the probabilities for EEL and PDI).

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[38] Using Eq. A4 from Ref. 14 (and similar ones for groups of three and four O_2 molecules), the total probability of finding either two, three, or four O_2 molecules adjacent to each other, forming an isolated group at a surface lattice site of an O_2-doped Kr matrix, is at most 0.05 for about 22% O_2, and 0.044 at 15% O_2.

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