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Non-adiabatic Curve Crossings in Dissociative Electron Attachment of Condensed O₂

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Abstract. Previously published data on electron stimulated desorption (ESD) from condensed O₂ or O₂ in solid matrices have been analyzed. Dissociative electron attachment (DEA) via the $2\Sigma_g^+$ resonant state can result in two different dissociation products (i.e. by proceeding to the dissociation limits $O(^3P) + O(^2P)$ and $O(^1D) + O(^1D)$). The $O(^1D)$ product requires dissociation via a non-adiabatic curve crossing. $O(^1D)$ is the dominant DEA product in gaseous O₂. Upon condensation, $O(^3P)$ becomes the dominant product; however, the branching ratio depends strongly on the kinetic energy of the dissociating atoms.

1. Introduction

Our previous theoretical findings concerning DEA of O₂ are summarized in Table 1. Of the many O₂⁻ states below 10 eV, only two states, i.e. the $2\Pi_u$ and $2\Sigma_g^+$ states, live long enough to dissociate yielding O⁻ ions. The other O₂⁻ states autoionize too fast [1]. The autoionization lifetime of the $2\Sigma_g^+$ state is predicted to be longer than that of the $2\Pi_u$ state [1]. The σ^- selection rule [2] forbids electron attachment to the $2\Sigma_g^+$ state directly from the ground state ($^3\Sigma_g^-$). To remove this restriction, the cylindrical symmetry of the O₂ molecule must be perturbed by its neighbors. The $2\Sigma_g^+$ state can however be reached directly from the first excited state ($^1\Delta_g$) even for gaseous O₂. Such a mechanism,



has been observed for gaseous O₂ and identified as such by Belic and Hall [3]. The $2\Sigma_g^+$ state is observed at 8.5 eV vertically above the O₂ ground state consistent with its predicted vertical energy of 8.1 ± 0.9 eV [1].

Table 1 Dissociative electron attachment mechanisms below 10 eV.

CHARACTERISTIC	MECHANISM		
	I	II	III
Symmetry	$2\Pi_u$	$2\Sigma_g^+$	$2\Sigma_g^+$
Elect. config.	$1\pi_u^{-1}1\pi_g^2$	$3\sigma_g^{-1}1\pi_g^2$	$3\sigma_g^{-1}1\pi_g^2$
Vert. E (eV)	6.0	7.7	9.0
DEA from g.s.	Yes	No	No.
Rel. Lifetime	smaller	larger	larger
Dissoc. limit ^a	1st	1st	2nd
Init. trajectory ^b	In	Out	In

^aThe 1st limit is $O(^3P) + O(^2P)$ and the 2nd is $O(^1D) + O(^2P)$.
^b"In" and "Out" refer to the initial movement of the O⁻ ion toward or away from the surface.

Belic and Hall [3] not only identified the $2\Sigma_g^+$ symmetry, but also found that the $2\Sigma_g^+$ state dissociates into the second lowest limit almost exclusively as indicated in Eq. (1) and Fig. 1. This implies a very high efficiency for a non-adiabatic curve crossing, since the lowest $2\Sigma_g^+$ state adiabatically dissociates to the lowest limit. The O₂⁻ adiabatic potential curves (see Fig. 1) calculated by Michels utilizing the MCSCF method [4], show an avoided curve crossing for the lowest $2\Sigma_g^+$ state and suggests a high efficiency for the non-adiabatic curve crossing because of the relative slopes of the two interacting curves.

Now, the question arises, what happens when the O₂ molecules are condensed or placed in a matrix? Does the lowest $2\Sigma_g^+$ state still dissociate predominantly to the second lowest limit, as it does in the gas phase?

2. The role of the surface

In the gas phase, the $O_a + O_b^-$ and $O_a^- + O_b$ dissociation limits of the homonuclear O₂⁻ molecule are degenerate, where subscripts (a and b) are used to differentiate the identical oxygen atoms. This degeneracy will be removed when an O₂⁻ is located on a polarizable surface and its symmetry

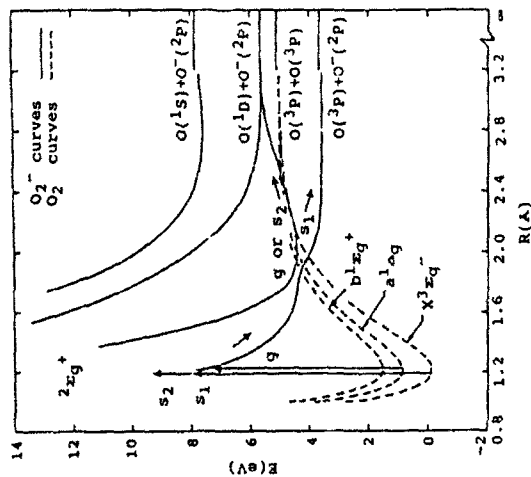


Fig. 1. Calculated potential energy curves for $2\Sigma_g^+$ states of O_2 [4]. The arrows indicate the dominate dissociation path in the gas phase (g) and in the solid (s) or condensed phase at 8 eV (s_1) and 9 eV (s_2).

dissociating fragments must break out of a "cage" which will slow down the dissociating fragments. Thus we expect the branching ratio to be altered in the condensed phase by both the relative slopes of the potential curves and the velocity of the dissociating fragments.

As seen in Table 1, three different mechanisms are identified yielding O^- with different electronic excitations, kinetic energies, and initial directions of motion. The singlet and triplet oxygen atoms [that is, $O(^1D)$ and $O(^3P)$] generally react with neighboring molecules quite differently because of the spin-conservation rule. This allows us to determine which product was formed upon dissociation, i.e. to answer the question whether the dissociation was adiabatic or nonadiabatic.

3. Results and Conclusions

We have examined a wide range of previously published and unpublished data involving O_2 condensed on rare gases and on Pt, and mixed gases (e.g. O_2 and CO, O_2 and N_2 , $^{18}O_2$ and $C^{16}O$ and O_2 with C_nH_n) of differing relative concentrations and thicknesses [8-11] with this question in mind. Application of retardation voltages gives some indication of the relative kinetic energies of the ions. These studies, much too lengthy to be described here, have produced the following conclusions:

- 1) The DEA of gaseous O_2 proceeds predominantly via the allowed mechanism I. Upon condensation of O_2 this mechanism appears to be suppressed with increasing thicknesses of O_2 , or increasing amounts of CO in the mixed gases. Since O^- anions via this mechanism initially move towards the surface of the O_2 film, requiring a "bounce" off the surface to be observed, the suppression is attributed to the increased probability of O^-/O_2 or O^-/CO interactions during the bounce.
- 2) Furthermore, the increased O_2-O_2 or O_2-CO molecular interaction breaks down the σ^- selection rule increasingly allowing the forbidden excitation to the $2\Sigma_g^+$ state. The forbidden mechanisms II and III become the principal contributors of O^- from solid O_2 or mixed gases.
- 3) The dissociation process of the $O_2(^2\Sigma_g^+)$ resonant state is significantly modified upon condensation. On the surface, the O_2 dissociates predominantly adiabatically into the lowest limit. This reversal from the gas phase is attributed to a 1 eV reduction in the energy difference of the two dissociation limits and resultant change in the relative slopes of the two curves.
- 4) In the sub-surface region, the $O_2(^2\Sigma_g^+)$ apparently also dissociates predominantly adiabatically to the lowest limit, but this is now

axis is not parallel to the surface. For the non-parallel case, the O_2^- state can dissociate into either $O+O^-/S$ or O^-+O/S where 'S' indicates the surface. The $O+O^-/S$ limit is lower than the O^-+O/S limit by a surface polarization energy. Regardless of the degeneracy, each O_2^- state must be connected uniquely to one of these limits. This connection between the O_2^- state and the dissociation limit can be determined by applying the Wigner-Witmer and non-curve-crossing rules [5]. The results obtained are shown in Table 1. Dissociation into the $O+O^-/S$ (O^-+O/S) limit implies that the O^- ion moves in (out) from the surface, and that some ions follow a "bounce" trajectory off the surface [6].

Within the Landau-Zener theory [7], the branching ratio at a curve crossing is determined by the relative slopes of the two curves at the crossing and the velocity of the dissociating ions at the crossing. Since at the surface, the two dissociation limits have different energy, the relative slopes of the two curves will be changed, and thus the branching ratio will be changed. In the sub-surface region, the polarization is expected to be more homogenous, in which case the energy spacing between the dissociation will not change significantly. However, in this case the

