Resonance Electron Scattering by O₂ Monolayers on Graphite: Reinterpreted

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Resonance Electron Scattering by O₂ Monolayers on Graphite: Reinterpreted

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1. Introduction

Both electron stimulated desorption (ESD) and inelastic electron scattering (IES) are enhanced strongly by anion resonant states. Occasionally, peak features observed in ESD and IES arise from the same anion resonant states. IED, however, unlike ESD, provides information on the symmetry of the anion resonant states through the angular distributions of the inelastically scattered electrons. Such electron angular distributions from O₂ on graphite have been studied extensively by Palmer and co-workers. Their results have been published in more than eight papers over the past four years [1-8] and summarized in two recent review articles [7,8].

On graphite, O₂ can be prepared in either the δ or 3 phase, where the molecules lie either parallel (δ phase) or perpendicular (3 phase) to the graphite surface [9]. The excitation profile of the X'(1Σg) state [10] shows two peaks at 6 and 14 eV for the 3 phase and just one peak at 8 eV for the 3 phase [7]. Palmer and co-workers assigned these 6 and 8 eV peaks to the same 3(1α) resonant state and attributed the 1-eV shift of the peak energies in the 3 and 3 phases to multiple electron scattering in the solid [3]. No assignment was made for the 14 eV feature. In this paper, we propose an alternative interpretation for the origin of the 6 and 8 eV peak and assign the 14 eV peak.

The 6, 8, and 14 eV peak features have been observed also in the ESD of O⁺ ions from O₂ films and O₂ on rare gas films, and attributed to 3(1α) (6 eV), 3(1α) (8 eV), and 3(1α) (14 eV) resonant states, respectively [10]. Excitation to the 3 and 3 states from the O₂ ground state is symmetry forbidden in the gas phase but is allowed in the condensed phase when the cylindrical symmetry of the O₂ is relaxed by interaction with the surrounding [11]. Recent ESD studies for O₂ clusters clearly demonstrated that the 8 and 14 eV peaks arise from the "symmetry-forbidden" states [12]. Furthermore, in the gas phase, the symmetries of 3 and 3 for the 6 and 8 eV peaks have been established experimentally based on the angular distribution of O⁺ ions resulting from electron impact on O₂ in the ground state and the 3 excited state respectively [13,14]. These assignments are completely in line with theoretical calculations [15] and analysis [11].

2. Origin of the 6, 8, and 14 eV peaks in the X=α excitation

The question here is: Do the 6, 8, and 14 eV peaks observed in the X=α excitation profile arise from the same 3(1α) (6 eV), 3(1α) (8 eV), and 3(1α) (14 eV) resonant states as those observed in the above experiments? We shall answer this question by examining the angular distributions of inelastically scattered electrons and the electron attachment selectivity observed by Palmer and co-workers [1-8].

3. The 3(1α) intermediate state in the solid

What happened to the 3(1α) state in the solid? In the gas phase, the X=α electronic excitation proceeds via the O⁺ ("1α") intermediate state at least for incident electron energies less than 5 eV [17]. This intermediate state should be differentiated from the O⁺ (14α) shape resonance peaked around 0.2 eV [18]. The latter has the 1α component primarily within the molecular region and a negligible amplitude outside this region, while the former has comparable amplitudes in both regions. Theoretical calculations [19]
predict that this non-resonant \( ^2\Pi_a \) intermediate state produces
a very broad peak (FWHM=10 eV), if there is one, in the X-a
excitation function.

The non-resonant \( ^2\Pi_a \) scattering, unlike the resonant \( ^2\Pi_a \)
scattering, is expected to be perturbed strongly when \( \sigma_2 \) \( ^2\Pi_a \)
condensed. In fact, there is ample evidence for quenching of
this non-resonant \( ^2\Pi_a \) intermediate state in condensed phase:
(a) The observed threshold energy (3.0 eV) is delayed by 2.1 eV
from the expected threshold energy of 0.9 eV [1, 20].
(b) The angular distribution of inelastically scattered
electrons at \( E_1=6 \) eV indicates \( ^2\Pi_a \) symmetry rather than
\( ^2\Pi_b \) symmetry, as was argued in Sec. 2.
(c) The observed features are too sharp (FWHM=4 eV) to arise
from non-resonant \( ^2\Pi_a \) scattering. The latter should have
either no peak or a very broad peak with FWHM=10 eV.
To sum up, the non-resonant \( ^2\Pi_a \) intermediate state is quenched
upon condensation and hence cannot be assigned to the 6 and 8
eV features.

4. Resonance energy shift due to multiple electron scattering
Palmer and co-workers offered two reasons for the 2-eV shift of
the \( ^2\Pi_a \) resonance peaks [3, 7]:
(1) theoretical calculations assuming the \( ^2\Pi_a \) symmetry and
(2) the similarity of the angular distributions for \( E_1=6.5 \)
and 8.5 eV.
Item (1): The assumption of the \( ^2\Pi_a \) symmetry is not valid as
argued in Sections 2 and 3. This explains partly why their
theoretical calculations did not agree well with the
experimental data [3, 7].
Item (2): Although the angular distributions for \( E_1=6.5 \)
and 8.5 eV are similar to each other for the \( \delta \) phase, those for the
\( \gamma \) phase are quite different. The only common feature between
them is that both decrease toward the normal direction.
In short, there is no evidence to support the 2-eV shift of the
\( ^2\Pi_a \) resonance.

5. A concluding remark
Palmer and co-workers assigned the 6 and 8 eV peaks, observed
in the X-a excitation, to the \( ^2\Pi_a \) resonance and attributed the
2-eV shift of the peak energies in the \( \delta \) and \( \gamma \) phases to
multiple electron scattering in the solid. Based on this
single investigation, they claimed that multiple electron
scattering can substantially shift resonance energies and
warned electron spectroscopists who study adsorbed molecules to
be aware of this possibility [3, 7]. Moreover, these authors
repeatedly suggested this possibility to explain experimental
results obtained by others [3, 8]. Because of the Palmer and
co-workers' claim, other authors considered (although did not
adopt) this possibility for an explanation of their results.
(21) This paper has demonstrated clearly that the Palmer and
co-workers' claim is unfounded at least for the cases studied
so far.

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