NEGATIVE ION RESONANCE ELECTRON SCATTERING FROM
ORIENTED, PHYSISORBED $O_2$

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ABSTRACT

The physisorption of diatomic molecules on a crystalline solid surface at low temperature provides a means of orientating the molecular axis and thus studying low energy electron scattering from an oriented molecule. The cross-section for vibrational excitation of one monolayer of $O_2$ on graphite at 25K has a peak near 9eV electron energy. The angular distribution of vibrationally inelastic electrons has been measured; comparison with calculated distributions, which include interference effects arising from multiple elastic electron scattering within the molecular layer, allows us to determine the orientation of the $O_2$ molecule on the surface and to identify the partial wave content of the resonance. The dominant partial wave (p$\pi$) is consistent with the $^2\Pi_u$ compound state but not the $^4\Sigma_u$.

Molecules can be bound on a surface in two ways:
(i) chemically (chemisorption), involving electronic charge transfer and often molecular dissociation - binding energies are typically a few eV;
(ii) by weak Van der Waals polarisation forces (physisorption), where the molecule adsorbs intact and without charge transfer (binding energies typically ~50meV).
In this paper we address the physisorption regime, where much of the molecular identity is retained, but the surface acts as a template which organises the molecules into two dimensional solid and fluid phases. Here there is a meeting point between the domains of atomic and molecular physics on the one hand and solid state physics on the other.

It has been known for some years now that the negative ion resonances which dominate the cross-sections for vibrational excitation of diatomic molecules in the gas phase by low energy electrons (≤20eV) [1] are also observed when the molecules are physisorbed [2-8]. What effects does the surface have? The attractive interaction between the temporary negative ion and its positive image in the (metallic) surface tends to lower the resonance energy by about 1eV [2,9], and also to decrease the resonance lifetime by lowering the centrifugal barrier [9,10]. Calculations by Gerber and Herzenberg [9] indicate also that the breaking of the inversion symmetry of a homonuclear diatomic molecule by the presence of the surface can allow partial waves of lower $l$ to be mixed into the wave functions of the incoming and outgoing electron waves which couple to the resonant state. The latter phenomenon parallels the difference in partial waves coupling to the $N_2$ $^2\Pi_u$ and CO $^2\Pi$ gas phase resonances, which is manifest in the different angular distributions of inelastically scattered electrons which are observed [1]. One would expect, then, that the experimental angular distributions obtained in the case of physisorbed molecules would prove a sensitive probe of the symmetry of the resonance on the surface. Here we present the first such measurements, for $O_2$ physisorbed on
graphite. We expect also that the angular profiles measured will reflect the orientation of the molecular axis on the surface, and hope indeed to be able to work backwards and derive the orientation from the angular distributions observed.

An electron can be added in various ways to the $3\Sigma_g^-$ ground state of neutral O$_2$ to form a negative ion. In the 6-11eV energy range where our angular measurements have been made, calculations for the isolated O$_2$ molecule [11] show two resonances intercepting the Franck-Condon region which can be formed by electron addition to the $3\Sigma_g^-$ ground state without violating the selection rules governing the attachment process [12]. These are the $2\Pi_u$ (Feshbach) resonance and the $4\Sigma_u$ (shape) resonance. The former has been assigned a dominant contribution to the dissociative attachment cross-section for both gas-phase [1] and condensed O$_2$ [13] - in each case the cross-section has a peak near 7eV. Wong et al [14], who observed a broad peak in the vibrational excitation cross-sections for gas phase O$_2$ centred near 9.5eV, reasoned that the dominant contribution to this enhancement was probably due to the $4\Sigma_u$ resonance. They thought a major contribution to the vibrational enhancement from the $2\Pi_u$ state was unlikely, given the lower energy of the peak in the dissociative attachment cross-section. For the purposes of our analysis of the vibrationally inelastic angular profiles presented later, we have treated both these resonant states as possible causes of the vibrational excitation.

When physisorbed on graphite at low temperatures, O$_2$ forms a whole range of different phases, depending on the number of molecules on the surface and on the temperature. The system has been the subject of extensive investigation by a variety of techniques which have provided details about the phase boundaries and the lattice parameters in the various phases. The reader is referred to a paper by Toney and Fain [15] for references to this work, and for a phase diagram. The phase we have studied is the $\zeta 2$ phase, prepared by methods described in detail elsewhere [16], the most dense monolayer phase. Molecular packing considerations, based on the lattice constants of the $\zeta 2$ phase and on the charge density distribution of the unperturbed O$_2$ molecule [17], suggest that the molecular axis in this phase is vertical or close to vertical [18], in contrast, for example, to the lower coverage $\delta$ phase for which a parallel orientation has been proposed [19]. The validity of this type of molecular packing argument can only be checked, however, by an experimental determination of the orientation of the molecular axis, something which has been lacking to date.

The experiments reported used a hemispherical electron monochromator and similar analyser. The monochromator was fixed on a flange but the analyser was free to rotate on a turntable. The graphite sample was mounted on a continuous flow helium cooled cold finger, also rotatable, and was resistively heated to ~1300K to remove contaminants from the surface prior to cooling and adsorption of O$_2$. Details of the sample stage may be found elsewhere [20]. The type of graphite used was Highly Oriented Pyrolitic Graphite (HOPG), an artificial material formed by cracking hydrocarbons over a heated substrate [21]. Crystals of HOPG have the advantage of being larger than single crystals of natural graphite, but the disadvantage of being polycrystalline, in the sense that they consist of crystallites typically 1µm in diameter, the c-axes of which are parallel to within 1°, but which have complete azimuthal disorder. For a single crystal, the hexagonal symmetry of the surface would lead to contributions to the electron scattering from six adsorbate domains; for HOPG, there will be contributions from a complete azimuthal range of domain directions.

An electron energy loss spectrum obtained from a monolayer of the $\zeta 2$ phase of O$_2$ on graphite can be seen in Fig. 1(a). The frequencies of the vibrational transitions labelled are in all cases close to the values in the gas phase, reflecting the absence of charge transfer in the physisorption interaction. This spectrum was obtained with an electron beam energy of 8.5eV, where the vibrational modes are especially strong, as Fig. 1(b) demonstrates. Here the intensity of the fundamental mode is plotted against electron beam energy, and shows a broad resonance centred at about 9eV. Previously [22], noting that the energy of this peak is about 0.5eV down from the gas phase peak, consistent with