

# INVESTIGATION OF POLAR ORGANIC ADSORPTION/DESORPTION FROM A MODEL CARBONACEOUS SURFACE: ACETONE ON GRAPHITE

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## 1. Introduction

Optical techniques have been widely shown to be convenient, *in-situ*, and real time methods to investigate surface processes.[1] Compared with conventional surface probes, such as ion and electron spectroscopy, optical techniques are useful over a wide range of ambient conditions.[2-4]

This study reports the adsorption and desorption of a model adsorbent representative of a volatile polar organic compound (acetone) on a model carbonaceous surface (HOPG). Many environmental phenomena involving carbonaceous surfaces occur under conditions where standard UHV surface science techniques cannot be applied, e.g., atmospheric pressure. ODR and TPD experiments were performed and showed that the strong correlation between ODR, determined in real time, and relative surface coverage, determined *a posteriori* by TPD for metal systems could also be extended to carbonaceous surfaces. Thus, we established that ODR could be used quantitatively to determine coverage on carbonaceous surface under conditions where TPD cannot be employed.

## 2. Experimental

A stainless steel ultra high vacuum (UHV) chamber, pumped by a turbomolecular pump backed by a mechanical pump, provides a base pressure of  $8 * 10^{-10}$  torr after bakeout. The adsorbent sample is highly oriented pyrolytic graphite (HOPG, grade SPI-1, SPI Supplies). A schematic view of the set-up of optics with UHV is provided in Figure 1. A Cu block, mounted on a stainless steel liquid nitrogen reservoir, holds two electrically isolated Cu rods as sample-support. The temperature is measured with a K - type thermocouple (chromel - alumel) spot-welded to one of the Ta sample fixing plates which is wedged against the sample. The sample was cleaved, using Scotch tape, immediately in air prior to installation. After the chamber bakeout, the sample was annealed at 1000 K overnight.

The chamber was equipped with an ion gauge and a quadrupole mass spectrometer (QMS, Stanford Research, AccuQuad300) to measure total and partial pressures in the chamber. The QMS was fitted with a stainless steel shield to ensure collection of molecules from the sample

alone during thermal desorption experiments.[5] The constant temperature ramping rate, typically 2.5 K/sec, is provided by a computer interfaced (LabView) power supply. Partial pressure, sample temperature, and ODR signals were monitored via a personal computer equipped with an A/D board controlled by a customized LabView program.

The light source for optical differential reflectance is a low-cost laser pointer. The laser beam passes through a polarizer and half wave plate on a rotatable mount, which allows the relative intensity of p- and s-polarized light incident on the sample to be adjusted. After reflection from the sample, the beam was divided into p- and s- polarized light via a polarizing beam splitter. Each component was detected separately by two commercially available photodiodes.

For the ODR experiments, the sample is initially cleaned by heating up to 600 K. The graphite is then cooled back to 91 K, and the intensities of reflected p- and s-polarized light are equalized by adjusting the half wave plate. Acetone is dosed while the ODR signal is monitored. After completing the desired dose of acetone, the temperature is ramped for desorption, while monitoring the ODR signal. The adsorption/desorption cycle is repeated to verify the reproducibility of the experiments. The experimentally measured normalized optical difference reflectivity (ODR) change,  $\Delta R/R$ , is defined by

$$\frac{\Delta R}{R} = \left( \frac{I_p - I_s}{I_p + I_s} \right) \quad (1)$$

where, R is the total reflectivity of clean surface and  $\Delta R$  is the reflectivity change due to adsorption and desorption.  $\Delta R/R$  is a complex function of the incident angle, as well as the optical properties of the adsorbate and substrate.[6-9]  $I_p$  and  $I_s$  refer to the intensity of p- and s-polarized light reflected from the substrate surface, respectively. Both these quantities are related to the reflectivity,  $I_s = R_s I_{os}$ ,  $I_p = R_p I_{op}$ , where  $I_{os}$  and  $I_{op}$  are the intensity of light incident on the surface and  $R_s$  and  $R_p$  are the reflectivity of s- and p-polarized light, respectively. The p-polarized light is the "signal" and the s-polarized light is used as the "reference" due to the fact that adsorbate-induced reflectivity changes depend on polarization, with p-polarized light being far more

sensitive than s-polarized light to the presence of adsorbates.[10]

## 4. Results and Discussion

The results of TPD experiments, for surfaces dosed with increasing acetone exposures, are shown in Figure 2, where the partial pressure of acetone (QMS signal) is plotted as a function of sample temperature. Each peak in the TPD spectra corresponds to the temperature of maximum desorption rate.

Each TPD feature is associated with molecules desorbing from different surface layers, in agreement with a literature report for acetone desorption from a graphitic layer on Pt(111).[11] The highest temperature peak (160-170 K) represents desorption from the monolayer.[6, 11] The second TPD peak (154-158 K) is associated with desorption from the bilayer.[11] The lowest temperature TPD peak (at about 145 K) represents desorption from the multilayer.[6, 11]

Figure 3 illustrates the growth of the TPD area of the monolayer and bilayer peaks calculated by deconvolution. The dotted lines are the fitting curves assuming that adsorption follows Langmuir kinetics. The bilayer peak begins to grow after the first layer has reached about two thirds of its saturation coverage. The similarity of the slopes of the Langmuir fits for both monolayer and bilayer indicates that the sticking probabilities of acetone on the HOPG surface and on the monolayer are similar. The appearance of the multilayer peak in the TPD spectra (Figure 2), at about 13 L, indicates the point at which molecules begin to adsorb on the bilayer. Again, the multilayer peak appears before the bilayer feature has saturated. The data clearly suggest that the adsorbates grow according to a Volmer-Weber mechanism rather than a layer by layer mode.[12]

The ODR signal is plotted as a function of acetone exposure scale in Figure 5. The near linearity of the ODR with exposure suggests that overall acetone adsorption on graphite does not follow simple Langmuir adsorption kinetics. However, the individual monolayer and bilayer states do follow Langmuir adsorption kinetics (see Figure 3). As can be seen in Figure 5, ODR signal increases linearly until about 7 L exposure (dashed line) at which point the bilayer has begun to grow and the slope of the ODR (solid line) becomes steeper. Even though the number available sites for adsorption on graphite decreases as the coverage increases, the actual adsorption surface area increases since the acetone layers themselves provide sites for acetone adsorption. Such behavior explains why the slope of the ODR signal and TPD area grow faster at higher coverage rather than saturating once the bilayer appears.

In order to validate ODR as a quantitative technique the optical reflectivity change should correlate with coverage as determined from TPD, for example. Figure 6, a plot

of the ODR signal as a function of TPD area, shows a linear correlation ( $R^2=0.995$ ) between these techniques. The correlation of the ODR signal and the TPD area suggests that ODR measures the surface coverage change induced by adsorption.

## Conclusion

The adsorption/desorption of a model adsorbent representative of a volatile organic compound (acetone) on a model carbonaceous surface (graphite) has been investigated under Ultrahigh Vacuum conditions. Optical differential reflectance (ODR) provides a sensitive, non-invasive, *in situ*, and direct probe of surface coverage during adsorption/desorption with real time resolution. TPD experiments show that acetone adsorbs in distinct monolayer, bilayer and multilayer states on graphite at 91K, suggesting Volmer-Weber growth rather than layer-by-layer growth mode. It is concluded that ODR is suitable to investigate carbonaceous surface kinetics induced by adsorption/desorption or any other phenomenon, resulting in a change in coverage, over a wide pressure range.

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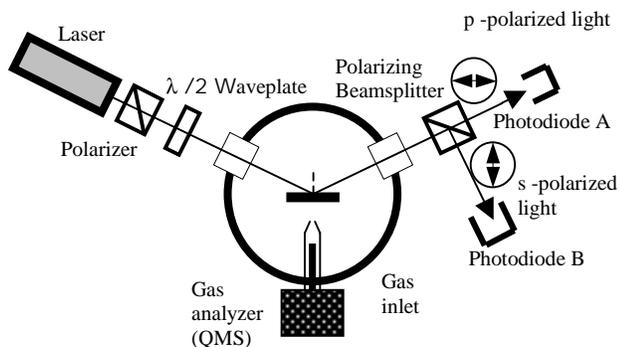


Figure 1. Schematic view of Optical Differential Reflectance (ODR) setup

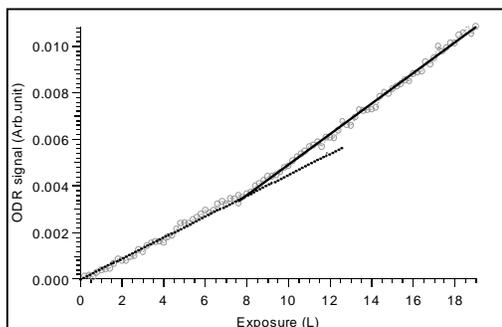


Figure 5. ODR signal as a function of acetone exposure.

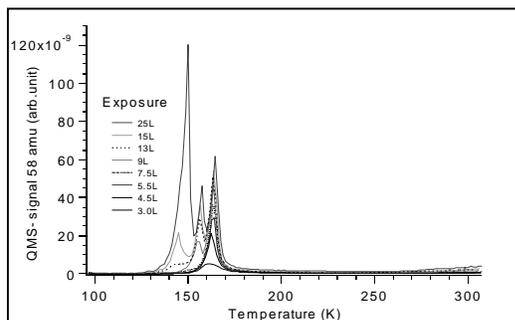


Figure 2. Temperature programmed desorption (TPD) spectra of acetone from graphite following adsorption at various acetone exposures at 91 K.

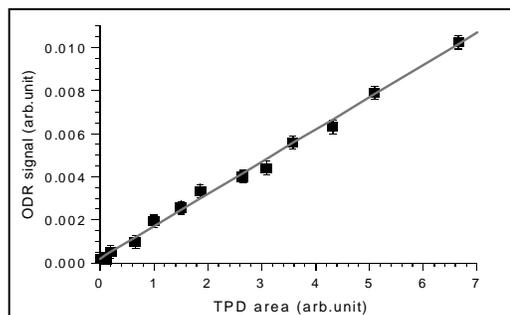


Figure 6. Correlation between ODR and TPD experiments for acetone adsorption on graphite. The solid line is a straight-line fit of the experimental data ( $R^2=0.995$ ).

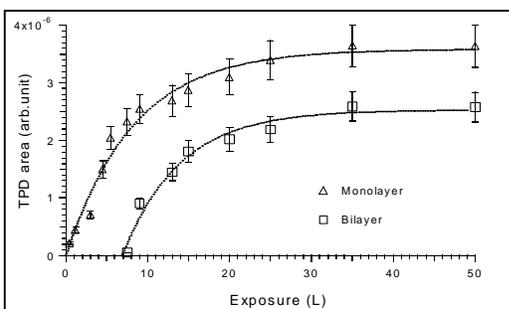


Figure 3. Integrated area of monolayer and bilayer of TPD features. The dotted lines are fits curve assuming the adsorption follows Langmuir kinetics.