I. INTRODUCTION

The study of species sorbed to surfaces is a daunting experimental problem. Numerous techniques have from time-to-time been developed which have provided information but few would suggest that our current state of knowledge is better than sparse. The classical techniques involve:

a) The measurement of vapour pressures of volatiles over surfaces as a function of temperature and mass of species sorbed and

b) Desorption (by pumping and heating) followed by chemical or physical analyses of the desorbed species.

Much more subtle methods have proliferated over the last few years including a wide variety of "electron" spectroscopies (e.g. secondary electron or Auger spectroscopy and ESCA), high resolution electron diffraction and L.E.E.D. and there is little doubt that their functions have contributed greatly to our understanding of chemisorption and some aspects of heterogeneous catalysis. Unfortunately, however, these methods rely on the use of highly evacuated systems and have almost inevitably led to an encouragement of the academic's tendency to *reductio ad absurdum*. Thus, it is intellectually attractive to study 'clean' single crystal surfaces and chemisorption thereto. The experimental methods listed above are ideal in this field and have therefore lead to an immense international investment in this type of research. It remains, however, that all catalytic processes of value, all corrosion or film problems in the real world, in fact surface chemistry is
concerned with species sorbed to dirty surfaces under relatively high pressure conditions.

There is no doubt that this field is considerably more complicated than that of the study of adsorption under high vacuum. The systems themselves (e.g. oxide catalyst surfaces, polymer layers or electrode systems) are difficult to define. Adsorption normally occurs in the presence of other major components and the chemistry which takes place on them frequently occurs at atypical sites on the surfaces. Physical methods viable in this field are scarce but infrared absorption spectroscopy has become a classic. Thus, almost every surface laboratory of significance, all large-scale catalyst producers and users find it essential to use this method. The applications are manifold and two excellent books and innumerable reviews have appeared surveying the field.

Infrared Absorption Spectroscopy of Surfaces

All materials absorb in the infrared region of the electromagnetic spectrum. They do so when, under appropriate conditions, molecular vibrations resonate with the illuminating radiation. Since molecular vibrational behaviour is itself complex, the infrared absorption spectrum constitutes an excellent fingerprint and can be used as a valuable qualitative and quantitative analytical method. See Figure 1. Further, the environment in which a molecule finds itself subtly affects its vibrational behaviour and this too "shows up" in the infrared spectrum. Thus, the attraction to the surface chemist is obvious — sorption of a molecule on a surface can lead to a spectral analysis identifying the sorbate, its decomposition fragments and the creation of permanent or temporary surface layers. In favourable cases, the spectrum will indicate changes of the surface caused by sorption and/or the mode of sorbate-sorbent interaction. Like all experimental methods, infrared absorption has its limitations and it is these that have lead to the research reported here.

The basic infrared absorption experiment consists of