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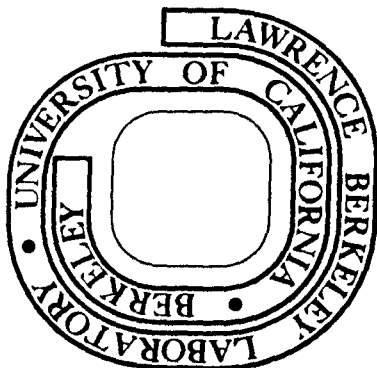
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A Coordination Chemist's View of Surface Science

By E. L. Muetterties^[*]

Structure, a necessary element for an understanding of chemistry, has not been precisely defined, in molecular detail, for the surface species formed at a solid-gas interface. Dramatic advances in theory, instruments and experimental procedures have now provided the surface scientists with an impressive arsenal of structural and electronic probes. Chemistry in the form of the classic displacement reaction can also provide an insight to the structure of surface compounds. In fact, many of the experimental procedures and systematics of the coordination and organometallic chemist can be effectively utilized in a complementary fashion with surface physics techniques to gain a more definitive picture of chemisorption states and reactions at a surface.

1. Introduction

A molecular understanding of chemical processes that occur at surfaces is essential to the advancement of science and technology in many diverse areas of surface science such as adhesion, corrosion, electrochemistry, catalysis and soil chemistry^[1a]. Despite major theoretical and experimental advances during this century, especially in the last fifteen years^[1b], the chemisorption process at a gas-solid interface remains a somewhat vaguely defined phenomenon in a structural context. Lack of a single definitive and general structural technique for the chemisorbed states has been and is still the major reason why a more precise molecular definition of chemisorption processes has not been realized. There are no precise analogs in the surface scientist's repertoire of physical techniques of the molecular chemist's three-dimensional X-ray analytical and nuclear magnetic resonance techniques, which so accurately and quickly limn the essential structural and stereochemical details of molecules. Advances in surface physics techniques have been especially impressive during the last decade notably in low energy electron diffraction^[2] and angle resolved photoemission spectroscopy^[3]. However,

none of these techniques has the incisive and general applicability for full structural determination of the molecular chemists' three-dimensional X-ray analysis. Accordingly, surface scientists often must rely upon a complimentary set of data from many different physical measurements in order to infer the full molecular features of the chemisorbed state. Some of these techniques can be *relatively* simple in application and others presently require a dedicated experimental arrangement. Important among the former set are Auger spectroscopy^[4], which can yield an elemental analysis of a surface, low energy electron diffraction^[2] which can sense the ordering of metal atoms and of chemisorbed species at a surface, and mass spectrometry which samples the gas phase above the surface. An important new technique among the "dedicated" set is high resolution energy loss spectroscopy (HRELS)^[5] which analyzes electrons inelastically scattered from a surface and which can provide vibrational information about chemisorbed species. A lexicon of common surface physics techniques is presented in Table 1.

Presently, a *structural interpretation at the molecular level* of data obtained from surface physics techniques is a nontrivial experimental and theoretical exercise. For example, low energy electron diffraction (LEED) data are difficult to interpret in precise and full structural detail at the molecular level. There are five distinct processes that must be considered in the

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Table 1. Lexicon of common surface physics techniques.

Technique	Principle	Application	Sensitivity (monolayer)	Penetration depth
Auger electron spectroscopy (AES)	Stimulated (typically electron stimulated) emission from valence or inner shell creates an excited ion. Auger electron is emitted in the deexcitation of the excited ion	Analysis of surface composition and electronic features	10^{-2} — 10^{-3}	1—7 layers
Ion scattering spectroscopy (ISS)	Energy loss for rare gas ion scattering from a surface reveals the mass of the surface atom involved in the scattering process	Analysis of surface composition	$\approx 10^{-3}$ — 10^{-4}	1 layer
Secondary ion-mass spectroscopy (SIMS)	Ion (typically rare gas ion) stimulated secondary ion emission	Analysis of surface composition	$\approx 10^{-6}$	1 layer
Ion neutralization spectroscopy (INS)	Incident low-energy ions are neutralized by electron transfer from surface atoms which then stimulate an Auger electron emission	Analysis of surface composition and valence band structure	10^{-2}	1 or > 1 layer
Electron spectroscopy for chemical analysis (ESCA)	X-ray stimulated electron emission from valence and inner shells of surface atoms	Analysis of surface composition and of surface atom oxidation states	$\approx 10^{-1}$ — 10^{-2}	1—7 layers
Ultraviolet photoelectron spectroscopy (UPS)	Ultraviolet radiation stimulated electron emission from valence shell of surface atoms	Electronic structure and orientation of chemisorbed molecules	10^{-1} — 10^{-2}	1—3 layers ≈ 1 layer in synchrotron radiation mode
Low energy electron diffraction (LEED)	Elastic scattering of low energy electrons from the surface and the near surface atoms	Symmetry features of surface atom environments, unit cell dimensions, and structural features of the surface	$\approx 10^{-1}$ — 10^{-2}	1—7 layers
High resolution electron loss spectroscopy (HRELS)	High resolution analysis of energy loss in inelastically scattered electrons from a surface	Analysis of vibrational states	10^{-2}	1—7 layers
Appearance potential spectroscopy (APS)	Programmed escalation of incident electron energy with scanning of the resultant X-rays from the surface	Analysis of surface composition and electronic features	10^{-2} — 10^{-3}	1—7 layers

theoretical analysis^[6] and a key consideration is the change in the potential function near the surface. Relatively definitive^[7] structural interpretations of diffraction data have been achieved only for the case of chemisorbed atoms on a metal surface^[8], and the only "molecular" chemisorptions to receive detailed analysis are those of acetylene on Pt(111)^[9] and carbon monoxide on Ni(100)^[10]. With recent experimental and theoretical advances^[3], angle resolved photoemission spectroscopy can be employed to assess the orientation of chemisorbed molecules like CO, NO and CN on a "flat" metal crystal. Extensions to molecules of greater complexity are feasible but nevertheless more difficult. The low energy electron diffraction and angle resolved photoemission studies are complementary, with the former primarily sensitive when operated in the normal incidence mode^[11] to distance parameters (distance between metal surface layer and the center of gravity of the chemisorbed molecule) and the latter very sensitive to the orientation of the chemisorbed molecule with respect to the metal surface plane. Both techniques have identified the same basic structures for sulfur atoms on Ni(100) (sulfur on four-fold sites within bonding interaction of four nickel atoms)^[12, 13] and carbon monoxide on Ni(100) (carbon sitting atop individual nickel atoms)^[10, 14]. Other techniques, now under study and development, should dramatically improve the arsenal

of surface techniques, *e. g.* ellipsometry for electronic and vibrational analysis, acoustical spectroscopy, surface sensitive (Auger-like electron) extended X-ray absorption fine structure, electron stimulated desorption, reflectance infrared and small angle neutron scattering.

Surface chemistry in its state of molecular development only ten or so years ago was rather analogous to the state of coordination chemistry at the turn of the century when no spectroscopic or diffraction techniques of structural significance were available. At that time, *Werner* in Germany^[15] and *Chernyaev* in Russia^[16], by utilizing chemistry that included displacement reactions, began to correctly infer stereochemical and structural features in coordination complexes. (This comparison is really invalid or at least unfair because the coordination complexes were susceptible to isolation and elemental analysis, and because resolution of enantiomers was feasible and was effectively utilized in the stereochemical studies.) There can be a similar utilization of the displacement reaction^[17] in surface science, and, with the modern ultra-high vacuum chamber, the chemistry of individual single crystal metal faces can be explored. The displacement reaction, guided by analogy to established coordination chemistry, and of course supplemented with data derived from surface physics techniques could assist the advancement of the state of molecu-

lar structural knowledge of chemisorption processes. The potential of such a combined chemical and physical approach to surface science is described in this article. Analogy to coordination chemistry is utilized to structure the discussion and to incisively define critical regions where the analogy itself breaks down.

2. Terminology and Boundary Conditions

All the surface chemistry described below is referenced to a rather idealized world of surface science, a world far removed from the physical conditions that prevail under most practical surface science conditions. It is the world of ultra-high vacuum, $\approx 10^{-9}$ to 10^{-12} torr, the interface between a metal and a near vacuum. Experimentation in this area has been enabled by dramatic advances in vacuum technology^[18]. There is a sound scientific basis for beginning with this idealized world. A pristine metal surface is a well defined starting state. The conditions which are essential to chemical studies of a clean metal surface can be realized only with the modern ultra-high vacuum chamber, and techniques, especially those based on electron diffraction and electron or photon spectroscopy, can be routinely applied to the chemisorbed state under these conditions. Although the extreme reactivity of a metal surface requires the clean ultra-high vacuum conditions, the chemistry of the surface can be explored under more conventional conditions. With a cell that may be lowered and raised so as to isolate the metal crystal from the vacuum chamber^[19], it is feasible to effect chemical reactions, for example catalytic reactions, at the same metal surface under atmospheric or superatmospheric conditions and at virtually any temperature without major contamination of the main vacuum chamber and then later reexamine the metal crystal under high vacuum conditions by surface physics techniques^[20]. The small area of the crystal face (about 0.5 cm^2) presents no problem today for the chemical studies because modern gas chromatographic and mass spectral techniques need only infinitesimally small amounts of material. The metal may be in virtually any physical form, a film, dispersed particles on a support, or a single crystal. Single crystals offer distinct advantages. A systematic investigation of the surface chemistry of the individual low Miller index faces as well as the high Miller index faces can identify the surface sites of low and high reactivity (see Fig. 1). It is also possible to selectively block different sites with foreign atoms as a further check of reactivity sites. The gap between ultra-high vacuum surface science and "real world" surface science can be and is being bridged today^[21].

Chemisorption processes at metal surfaces typically are divided into two major groups: (i) associative processes in which there is no fragmentation of the molecule and (ii) dissociative processes in which bonds in the molecule are broken on chemisorption to give chemisorbed species that are molecular fragments. The paradigmatic dissociative process is that of chemisorption of hydrogen on transition metal surfaces to give hydrogen atoms which are bonded to metal atoms, *i.e.* to form metal-hydrogen bonds. The partitioning of chemisorption processes into associative and dissociative processes faithfully follows surface science terminology but the terms may convey to chemists a different and improper aspect of reaction mechanistic information. Unfortunately, the coor-

dination chemist characteristically employs the terms dissociative and associative quite differently in a reaction mechanistic context^[22].

For the individual classes of chemisorption, I shall employ as a partitioning scheme the types of reactions established in coordination and organometallic chemistry and will reference the discussion of surface chemistry to that of the coordination chemistry of zerovalent or low-valent transition metal chemistry.

3. The Surface Experiment

Since there will be extensive reference to the displacement reaction using metal single crystals in an ultra-high vacuum chamber, a brief description of equipment and procedure is presented here.

The single crystal of the desired orientation may be shaped^[23] from a large crystal to the appropriate dimensions, *e.g.* a 5 mm diameter disk with a thickness^[24] of about 1 mm and polished by a combination of mechanical, electrochemical and chemical procedures. The orientation is checked with the Laue X-ray diffraction pattern. If for example, the desired surface is a (111) face of a hexagonal close packed metal, the vast majority of the metal atoms will, in fact, reside in a pseudo-hexagonal environment after appropriate annealing of the crystal in the vacuum chamber. However, the surface is unquestionably heterogeneous. If viewed microscopically, the crystal will clearly display scratches and defects. Also there will be steps (see Fig. 1). The crystal will not be perfectly

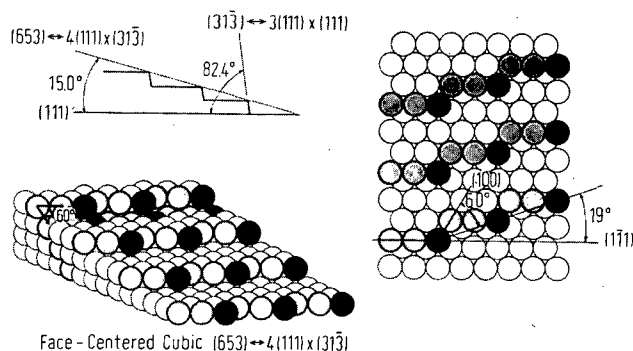


Fig. 1. A representation of a high Miller index plane for a face-centered cubic metal structure in which there are discrete areas described as: (i) "terraces", which are (111) sections with surface metal atoms (unshaded circles) that have a coordination number of nine, *i.e.* nine nearest neighbor metal atoms; (ii) "steps", where the metal atoms (light shading) have a coordination number of seven; and (iii) "kinks", where the atoms (dark shading) at the leading edge have a coordination number of six. (This drawing was prepared by Ms. Carol E. Smith at Berkeley.)

flat; a helium beam scattering experiment would show only 30–60%^[25] of the surface atoms to be in the same plane. However, these deviations from ideality do not appear to be severe limitations in the final analysis if there is a systematic chemical study of crystal faces. It is critical to underscore the point that many of the surface physics techniques that directly address the issue of structure focus primarily on the ordered structure and "ignore" the disordered structure—a point that surface scientists explicitly acknowledge but one that the casual reader of surface science literature may tend to either miss or forget.

After the orientation check by X-ray crystallography, the crystal is then welded either directly to metal support rods (the same or different metal) or to a metal (*e.g.* tantalum) backing to which is then welded tungsten wire and attached to insulated supporting rods^[26]. The former arrangement provides a means of electrical resistance heating whereby all the current passes through the crystal and the latter an indirect heating arrangement with most of the electrical current passing through the metal backing^[27]. Alternative mounting configurations have advantages in specific applications. A photograph of a mounted crystal is shown in Figure 2. The mounted crystal is then attached to the manipulator and inserted typically through the top port of the vacuum chamber (Fig. 3 and 4). The manipulator has rotational and translational degrees of freedom to allow for proper positioning of the crystal for individual experiments.

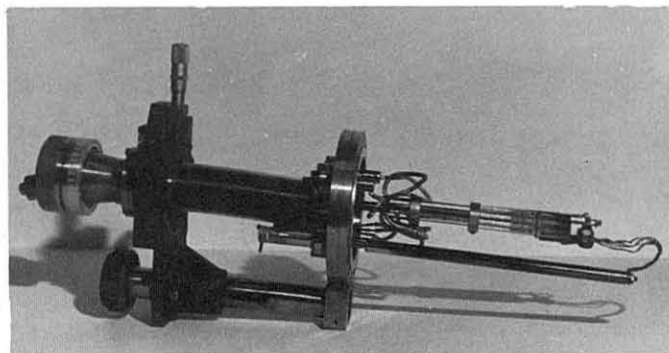


Fig. 2. Photograph of a metal single crystal mounted on a manipulator (from the laboratories of Prof. Robert P. Merrill). There are many possible variations in the mounting and peripheral features such as the heating element for the crystal. The arrangement illustrated here has a shielded cup that can be heated by an electron gun and thereby indirectly heat the crystal. Because the typical metal crystal has a very small volume, no significant thermal gradient across the crystal exists even at quite elevated temperatures. By modification, it is possible to cool the metal crystal to temperatures below 65 K. Temperature control and measurement can be quite precise. The depicted crystal manipulator effects controlled translational as well as meridional and azimuthal rotational degrees of motion of the crystal. (This photograph was kindly provided by Mr. Herbert Sawin.)

After opening the chamber to emplace a crystal, an extended chamber reconditioning period is required. A bakeout at 500–550 K for a period of two days is typical. At this point, cleaning of the crystal can begin. The crystal is not only contaminated on the surface but also internally and these trace bulk impurities are potential surface contaminants. Very high initial bulk purities of six “nines” can lead to low surface purities if there is any tendency for segregation of impurities at the surface when the crystal is heated. The number of surface atoms in a metal crystal is about 10^{15} per cm^2 as compared to a bulk density of about 10^{22} atoms per cm^3 . If there were 0.0001% carbon impurity in the bulk and if there were a high degree of segregation at the surface, then the metal crystal could have a full monolayer of carbon on the surface after an annealing treatment. Thus, the metal crystal must be subjected to a stringent purification procedure.

Details of crystal cleaning procedures and the characterization of surface states often are not fully presented in the surface science literature^[28]. Crystal cleaning procedures are recipes based on the crystal chemistry, the chemistry and the impurity segregation features peculiar to each metal. A

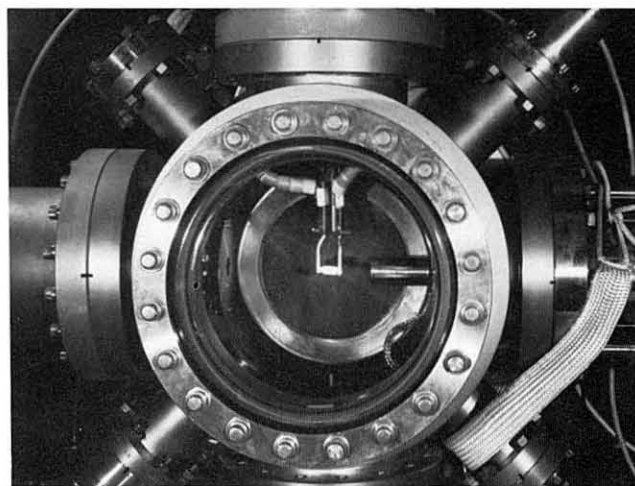


Fig. 3. A close-up photograph of an ultra-high vacuum chamber. In direct line of sight is the viewing port and within the chamber and in the center can be seen the metal crystal. Directly to the left of the crystal is the inlet to the mass spectrometer and to the right is an evaporating element for coating the metal surface by sublimation. To the 1:30 o'clock position is the glancing incidence Auger electron gun, the 4:30 position the leak valve connection and the 7:30 position the ion gun for ion sputtering experiments. To the rear is the low-energy electron diffraction screen and, hidden from view by the crystal, the electron diffraction gun which is at the center and to the rear of the screen. At the top and out of view is the crystal manipulator. (This photograph was kindly supplied by Prof. G. A. Somorjai.)

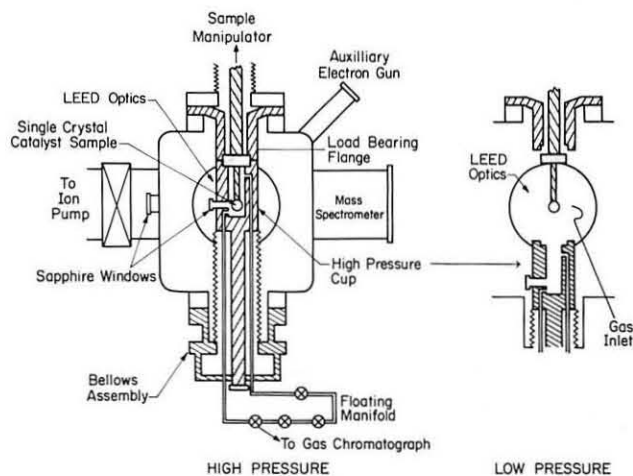


Fig. 4. A schematic drawing of a vacuum chamber, equipped with an isolation cell, and the peripheral equipment (courtesy of Prof. G. A. Somorjai). To the left is the schematic of the high pressure configuration and to the right the high vacuum configuration with the isolation cell lowered.

conventional cleaning procedure consists of ion (charged argon ion) sputtering of the surface at some temperature whose upper limit is set by phase transitions or the melting point of the metal and impurity segregation characteristics and whose lower limit is set by impurity atom mobility. For example, the major impurities in nickel are sulfur and carbon. Essentially all the sulfur and some of the carbon can be removed by argon ion bombardment at 1000 K. Because the carbon has a substantial bulk solubility at 1000 K, it is not quickly removed by sputtering at these temperatures. Surface segregation is however substantial at 680 K and this is the optimal temperature for carbon removal. Total cleaning time for nickel is about twelve to twenty-four hours and although minor traces of carbon may remain in the bulk, the surface will be essentially clean.

Surface purity is established by an Auger analysis^[4] in which high energy electrons (1–5 keV) are directed at the metal crystal at grazing incidence angles or a normal incident angle (the conventional configuration of the low energy electron diffraction experiment)^[29] (Fig. 5). The ejected electrons in this experiment have a relatively short mean escape depth, *ca.* 5–20 Å, so that the analysis is largely a surface elemental analysis. Figure 6 shows an Auger analysis of a carbon-doped nickel(111) surface. The Auger analysis for many elements can be very sensitive but is only semiquantitative (factor of two at best) as commonly applied^[30].

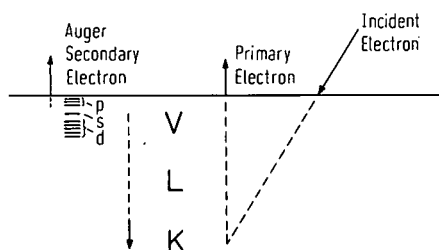


Fig. 5. A schematic representation of the Auger experiment. A beam of electrons or X-rays (1–5 keV) is directed at a surface. Electrons in the inner levels of an atom may be ejected if their binding energy is less than those of the incident beam. An electron vacancy created by this stimulation can be filled by a process in which an electron in a higher level drops into the vacancy. The energy released in this transition can be transferred to another electron (same or a different atom), which if its binding energy is less than the deexcitation energy transferred to it may be ejected into the vacuum. This secondary electron is the Auger electron and it has an energy characteristic that is a primary function of energy level separation in the ion. Thus an energy analysis of the emission electrons provides an elemental analysis of the surface. The emission escape depth of the Auger electron is a function of the energy and ranges from 1 to 7 atomic layers. The energy (energy shift) and the line shape (intensity *vs.* energy) can, in principle, provide electronic information about the environment of the atoms.

After a clean surface has been obtained and also defined by the Auger experiment, the surface must be annealed to correct surface irregularities that resulted from the crystal preparation and from ion bombardment^[31] in the cleaning process. For nickel metal, an annealing at 1000 K for about one hour is usually sufficient as judged by the sharpness of the low energy electron diffraction spots and the lack of diffuse background in the diffraction pattern.

At this point, with a clean, oriented crystal face, the chemisorption experiment can begin; but before describing the chemisorption experiment a few comments about the vacuum and the critical pumping scheme would be in order. The vacuum chamber may be evacuated with a diffusion pump provided that efficient cold traps separate the pump and the chamber, otherwise hydrocarbon vapor would contaminate the vacuum system. A high-efficiency ion pump and a titanium sublimation pump are frequently employed, whereby vacuums in the 10^{-10} to 10^{-11} torr range can be attained. At 10^{-10} torr, the major gaseous species are usually H_2 and CO. Unfortunately, chemisorption of H_2 and CO are significant processes on metals like nickel at these pressures. Hence the metal surface will be "clean" at such fluxes for a period of about 60 minutes assuming a unitary sticking coefficient for the residual gaseous impurities. It is highly desirable to further reduce this background pressure because the lifetime of the "clean" surface would be raised and because the study of displacement reactions would be simplified. Reduction of H_2 and CO background to the nondetectable (mass spectrometric)

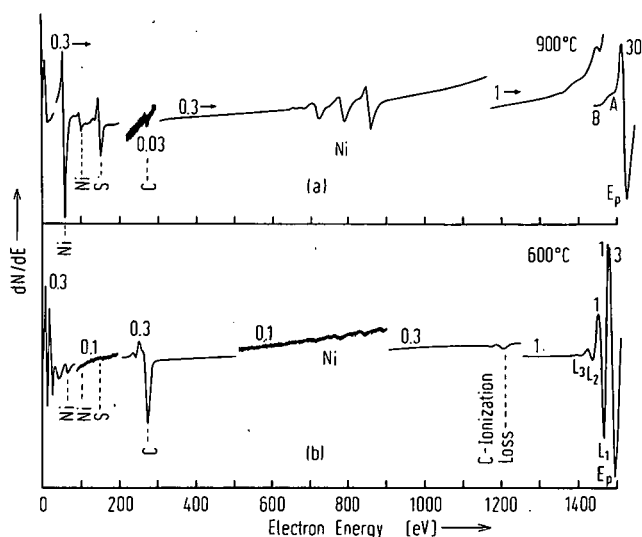


Fig. 6. Auger spectra from a nickel(111) surface, using a cylindrical mirror analyzer, which illustrates the phenomenon of impurity segregation in metals. The nickel specimen had been doped with carbon and there was a small sulfur impurity. a) This Auger spectrum is essentially that of a pure nickel surface at 900°C, the carbon impurity atoms are largely in the bulk. b) At lower temperatures, 600°C, there is a carbon segregation at the surface. The numbers 0.3, 0.03, etc. refer to sensitivity settings. The loss peaks L_1 , L_2 and L_3 (plasma losses) are equally separated (≈ 29 eV apart). (The spectra were kindly supplied by Prof. J. Blakely (cf. H. R. Pati, J. M. Blakely, *J. Appl. Phys.* 45, 3806 (1974)).

level requires some type of cryogenic pump or a liquid nitrogen-cooled sublimation pump, which coupled in parallel with a turbomolecular pump is an excellent pumping arrangement in terms of speed and effective vacuum. A good turbomolecular pump can quickly reduce the pressure in a chamber to 10^{-9} torr, at which point the cryogenic pump can then preside to further reduce pressure to the 10^{-11} to 10^{-12} torr level. This pumping configuration although not common today may be so in several years.

In the chemisorption experiment, the reactant molecule is slowly introduced through a leak valve from a glass or metal manifold into the chamber through a hollow metal needle^[32] directed at the crystal so as to minimize chamber contamination; alternatively an isolation cell may be employed to maximally limit chamber contamination. For less than a monolayer coverage of the metal crystal face, the exposure times required are a function of the flux of the molecule being introduced and the sticking coefficient for the molecule on the metal. With a near unity sticking coefficient, exposure times of 10–30 seconds are sufficient with quite low fluxes (10^{-9} to 10^{-10} torr pressure). This experiment is monitored with an ionization gauge and a mass spectrometer and optionally by the low energy electron diffraction pattern. The diffraction pattern has diagnostic value in that ordering of the chemisorbed layer usually will be evident immediately and, if not, the increase in background is a qualitative measure of the extent of coverage (Fig. 7). Care must be taken in electron scattering experiments to ascertain whether the electron beam itself may be affecting the structure of the chemisorbed species; the electron beam can damage the surface species. Auger electron spectroscopy provides the semiquantitative elemental analysis of the surface relative to the metal itself. At this point, a thermal desorption experiment, with the metal crystal face turned toward the inlet to the mass spectrometer, qualitatively measures the thermal reversibility

of the chemisorption process. In a reversible process, there is a regeneration of the clean metal surface and volatilization of the original molecule which can be so identified by its mass spectral pattern. If the thermal reactivity of the chemisorbed molecule is high relative to a molecular desorption process, the mass spectral analysis of gaseous desorption products will delineate the volatile decomposition products and an Auger analysis of the resultant surface will define the residual contaminant elements and their relative concentrations. The thermal desorption process^[33-35] also can be assessed semiquantitatively so as to establish the heat of the desorption process and the order of the desorption process through a study of the desorption profile as a function of heating rate.

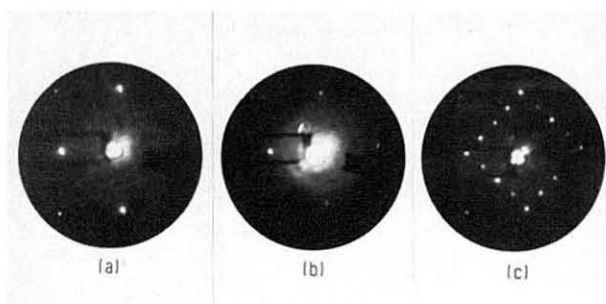


Fig. 7. a) A low energy electron diffraction pattern for a clean palladium(100) surface. The strong central spot is the zero level spot; three of the four first order spots can be clearly seen. b) Chemisorption of carbon monoxide at less than 0.5 monolayer yields a disordered chemisorption state on this palladium surface as shown by the much higher level of background in the pattern in the center; close inspection will reveal hazy higher order spots which demonstrate that there is some ordering of the carbon monoxide molecules under these conditions. c) Diffraction pattern for a half monolayer of CO on the Pd(100) surface. The pattern can be indexed as a centered (4 × 2) pattern rotated by 45°. This system was originally described by J. C. Tracy and P. W. Palmberg, *J. Chem. Phys.* 51, 4852 (1969). (These photographs were kindly supplied by Dr. S. D. Bader, Argonne National Laboratory and Prof. J. Blakely, Cornell University.)

In a displacement reaction, the following is the ideal protocol: The molecule to be displaced and the displacing molecule should contain at least one element not common to the other so that the Auger analysis of the surface before and after attempted displacement has an incisive qualitative significance^[36]. Ideally, the initial molecule should be chemisorbed on the metal surface with the metal crystal closed off from the major chamber by the isolation cell. With the metal crystal so isolated from the main chamber, the main chamber may be "lightly" preconditioned with the displacing molecule and then thoroughly evacuated. This procedure will maximize the possibility that the displaced molecule is generated from the metal crystal face rather than from the far reaches of the vacuum chamber. Then, the isolation cell may be removed and the introductory gas needle repositioned close to the metal surface. As the displacing gas is introduced through the needle, the system is monitored by mass spectrometry for detection of the original molecule if it is displaced. Finally, an Auger elemental analysis of the surface may be performed. In this manner, a semiquantitative analysis of the displacement reaction can be achieved. The displacement reaction may be effected at any temperature that is less than the temperature of molecular desorption or of some irreversible surface reac-

tion. Because surface temperatures can be minimized in displacement reactions, this chemical probe should be a more general one than thermal desorption; the problem of thermal reactivity can also be minimized^[36].

For the nonexpert, a measure of practical experimental time scales is noteworthy. The time required for a chemisorption experiment (after a clean surface has been achieved), the critically associated physical analyses (Auger and diffraction experiments) and a thermal desorption or chemical displacement reaction is about two hours. If, for example, a nickel(111) crystal is contaminated with carbon after these experiments, another 5–12 h of crystal purification procedure may be required. Practically speaking, the number of experiments per week per chamber is about three to seven for hydrocarbon-nickel(111) reactions. This number would be larger for iridium or tungsten which are easier to clean and substantially lower for iron which is extremely difficult to clean.

4. Classes of Chemisorption at a Metal Surface and a Chemical Approach to Characterization of these Classes

4.1. The Main Classes

Within the three main classes of chemisorption processes, associative, dissociative and polymerizative, there are many potential subclasses that are differentiated by reversibility, general structural features and molecular rearrangements^[36]. All these classes and subclasses have their analogs in coordination chemistry^[36]. I discuss first the three main classes of chemisorption reactions.

4.2. The Simple Associative Reaction Class

The conceptually simplest class of chemisorption processes is an associative and thermally reversible one in which the molecule is bound to one or several surface metal atoms with σ or σ - π bonds. For example, carbon monoxide chemisorbs on the (111) crystal face of platinum, and angle resolved photoemission data^[37] for the platinum and nickel(111) cases are best interpreted in terms of a more or less perpendicular orientation of the CO molecule with respect to the surface with metal-carbon not metal-oxygen bonding—*i.e.* structural and stereochemical features that would be anticipated by analogy to coordination chemistry. It is not known whether the carbon atom is centered on a metal atom (terminal position) or between two or three metal atoms (bridging position); all three possible stereochemistries, the terminal and two bridging positions are known in molecular metal carbonyl clusters (see Fig. 8). Chemisorption of carbon monoxide on platinum or nickel is thermally reversible. On heating a nickel crystal (111 orientation) with chemisorbed CO, the desorption of CO has been detected by the sudden pressure increase, and confirmed by mass spectroscopic analysis, at *ca.* 440 K. The desorption process, a first order process, yields an *upper estimate* of the Ni—CO bonding energy of about 25–30 kcal/mol which is very close to the average Ni—CO bond energy in Ni(CO)₄^[36].

To illustrate the potential of the chemical approach to surface science consider the specific example of acetonitrile chemisorption. Acetonitrile is a molecule characterized in transition metal coordination chemistry as a relatively weak ligand^[38]; it is a weak σ donor and π acceptor. In contrast, CO, a weak σ donor but strong π acceptor ligand, is a relatively

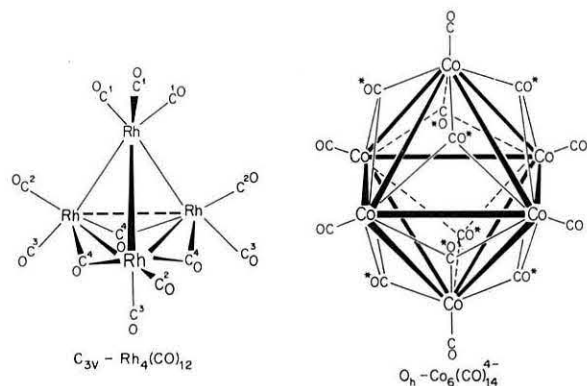


Fig. 8. Molecular geometry of the clusters $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_6(\text{CO})_{14}^{4-}$, which, respectively, have idealized C_{3v} and O_h symmetry. In the former, there are four types of CO environments denoted by superscripts. One set comprises bridging carbonyl groups, superscript 4, which are C-bonded to two rhodium atoms. In $\text{Co}_6(\text{CO})_{14}^{4-}$, there are six equivalent terminally bonded CO groups and eight triply bridging CO groups that are centered over the faces of the Co_6 octahedron. For crystallographic details see C. H. Wei, G. R. Wilkes, L. F. Dahl, *J. Am. Chem. Soc.* 89, 4792 (1967); V. G. Albano, P. L. Bellon, P. Chini, V. Scatturin, *J. Organomet. Chem.* 16, 461 (1969).

strong field ligand for zerovalent or low valent metal atoms. This characterization of CH_3CN and CO in coordination chemistry is nicely reflected in metal surface chemistry. For example, CH_3CN is weakly chemisorbed on the $\text{Ni}(111)$ surface at 300 K and is reversibly desorbed at 360 K^[36]. The estimated upper limit bond energy for the surface CH_3CN —Ni bond is 18—22 kcal/mol, a value substantially lower than that for carbon monoxide^[36, 39]. Most importantly, it has been shown that carbon monoxide easily displaces acetonitrile from the nickel surface, a process monitored by mass spectroscopy to show that the acetonitrile is actually displaced as the CH_3CN molecule. Auger analysis demonstrated that the resultant surface was free of nitrogen (CH_3CN) after the CO displacement reaction^[36, 39].

Another type of chemical experiment demonstrated that CH_3CN was not rearranged to CH_3NC in the chemisorbed state on nickel^[39]. The isocyanide, CH_3NC , is a very strong field ligand in zerovalent or lower valent transition metal coordination chemistry and in molecular displacement chemistry; isocyanides generally displace CO readily from coordination complexes. As expected then by this analogy, CH_3NC was strongly chemisorbed on $\text{Ni}(111)$ and could not be displaced by either CH_3CN or CO ^[39]. From this finding, it can be concluded that CH_3CN is not rearranged to CH_3NC , or *vice versa*, in these chemisorbed states. This chemical technique of utilizing structural isomers can be exceedingly valuable in establishing qualitative structural and stereochemical information about the chemisorbed state.

The structure of the chemisorbed state for CH_3CN on $\text{Ni}(111)$ is not established. It is believed that the molecule is normal to the surface. Low energy electron diffraction studies show an ordered state; there is a (2×2) pattern which indicates

that the unit cell of the ordered surface structure is twice that of the nickel surface structure and that in a rotational context the surface structure is aligned with the metal surface structure (Fig. 9)^[37]. In principle, an analysis of the intensity

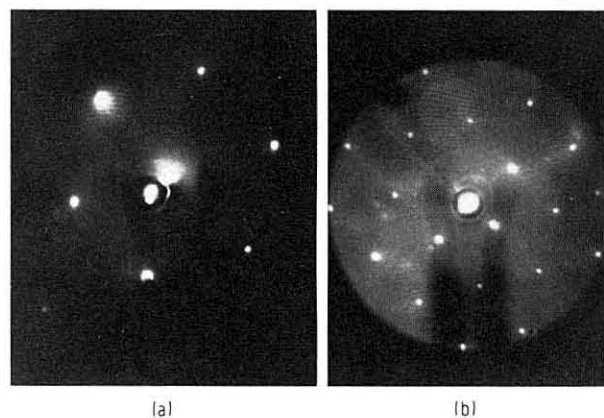


Fig. 9. a) Normal incidence low energy electron diffraction pattern for the face centered cubic nickel(111) crystal face. The large diffuse central spot is the zero order spot. In the ring of six spots, the real three-fold symmetry is qualitatively in evidence for these first order spots. b) (2×2) ordered pattern for CH_3CN on this nickel(111) surface taken at the same electron energy and a nearly identical perspective. All the first order nickel spots except two (to the right) can be seen and at half order positions are the additional spots that established the (2×2) pattern. The unit cell of the CH_3CN ordered structure is twice that of the nickel unit cell. The furrow patterns on the right are not fingerprints but are reproductions of the screen texture.

variation of the diffraction spots with change in incident electron energy could provide a structural characterization, but a definitive analysis would be very difficult. In point of fact, the size of the chemisorbed CH_3CN unit cell is a very important piece of information—it virtually requires that the molecule be normal to the surface; it cannot be linear and parallel to the surface. Considering the van der Waals' radii, it is not possible to place a perpendicularly oriented acetonitrile molecule above each nickel atom—but it is possible to place one molecule over every other nickel atom. This would then generate a (2×2) cell (also consistent with the diffraction data would be a displacement of the CH_3CN lattice so as to place the nitrile molecules in bridging positions; see Fig. 10).

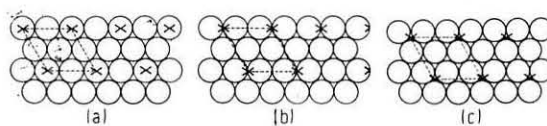


Fig. 10. Superimposed on the close-packed array of spheres representative of the (111) face of nickel are marks (X) that denote three of the symmetry limiting positions for CH_3CN molecules in the (2×2) chemisorbed state of CH_3CN (presumed to be normal to the surface). There is an infinite array of possible (2×2) structures because the only constraint here is a rotational correspondence between the lattices representative of the nickel atoms and of the chemisorbed acetonitrile molecules.

One might ask whether CH_3CN actually dissociatively chemisorbs—to give for example CH_3 and CN chemisorbed species. This specific possibility appears unlikely because it was demonstrated that the chemisorption of cyanogen $(\text{CN})_2$ on nickel(111), where CN chemisorbed species are presumably

formed, is an irreversible process^[39]. Cyanogen chemisorbed on a nickel(111) face is very strongly bound and thermally reacts above 770 K to evolve nitrogen gas^[39].

An alternative and definitive chemical probe for detection of dissociative chemisorption processes is isotopic labeling. Thus, in the case of acetonitrile, chemisorption of a mixture of CD₃CN and CH₃¹³CN would not be expected to yield any CD₃¹³CN molecules on thermal desorption (a doubly labeled ¹³CO—C¹⁸O experiment can be employed to detect reversible dissociative chemisorption of CO).

This limited and very simple study of CH₃CN and CO chemisorbed on nickel illustrates the potential of the displacement reaction for a characterization of the nondissociative, molecular class of chemisorption. A systematic study based on the displacement reaction should establish a ligand field strength series referenced to the various transition metals. It is anticipated that any nondissociative or molecularly chemisorbed molecules should be subject to displacement by another molecule, if (i) their heats of chemisorption are not too disparate and (ii) the molecule is not rearranged or extensively rehybridized on chemisorption. In the first qualification, the constraints are not too severe because a thermodynamically unfavorable displacement reaction can be driven readily on a mass action basis in surface chemistry: the partial pressure of the displacing molecule can be varied over an enormous range, *e.g.* a pressure change by six orders of magnitude is a feasible change for an experiment. The second qualification relates to structural information and is nicely illustrated for the case of acetylenes and olefins.

Olefins or acetylenes bound to a single metal atom in a coordination complex are readily displaced by other molecules and the limited calorimetric data indicate that the metal-olefin bond energy is slightly less than the metal-carbon monoxide bond energy in a zerovalent transition metal complex^[40]. Chemisorption of either acetylene or ethylene is not an especially exothermic process on copper and is probably endothermic on silver. The bonding of a molecule like ethylene on a copper surface may be a weak σ - π interaction analogous to the Dewar-Chat-Duncanson model^[41] (Fig. 11) of π bound

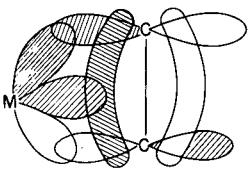


Fig. 11. Qualitative representation of the orbital interaction of the π and π^* orbitals of an olefin with the acceptor and donor orbitals of a transition metal as originally presented by Dewar and by Chatt and Duncanson [41].

olefins in coordination complexes. The story for nickel metal is quite different. Acetylene, ethylene, propylene, and 2-butylene are all irreversibly chemisorbed on the nickel(111) face; attempted thermal desorption yielded only hydrogen desorption peaks at about 370 K^[37]. Clearly these molecules are not simply bound in a σ - π fashion at single metal atoms at the surface of the metal. There remain two possibilities. These unsaturated molecules may be bound to two or more surface metal atoms by relatively strong σ metal-carbon bonds with an extensive rehybridization at the "unsaturated" carbon atoms of the acetylenic or olefinic molecule. Alternatively,

these molecules may chemisorb with concomitant cleavage of C—H bonds to give molecular fragments that individually are no longer susceptible to a displacement reaction. Distinction between these two possibilities remains a major challenge in surface chemistry for it is directed to a very important general class of surface reactions.

It is desirable to effect displacement reactions at relatively low temperatures to avoid complicating side reactions derived from thermal reactivity of the chemisorbed molecule. Some displacements at a metal surface will proceed at room temperature and slightly below. Thus the activation energy for displacement can be as low as 15–20 kcal/mol. If the activation energy for chemisorbed molecules that contain C—H bonds were to exceed *ca.* 40 kcal/mol, the displacement reaction may not be effective because dehydrogenation, cleavage of carbon-hydrogen bonds, of the molecule will have an activation energy of this magnitude. These points raise interesting questions about the mechanistic details of the displacement reaction but there is no substantive information. For the time being, we may envisage a displacement reaction using a localized surface model. If a displacing molecule chemisorbs in a vacant site adjacent to the initially chemisorbed molecule there *may* be a weakening of the binding for the latter—chemisorption of another displacing molecule in another nearby site may then be sufficient for the displacement of the original molecule. For a flat metal crystal, associative^[22] (bimolecular) displacement reactions at a single metal site are improbable simply because of geometric constraints.

4.3. The Simple Dissociative Reaction Class

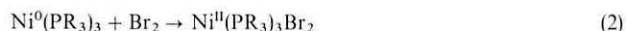
Many diatomic molecules, X₂, chemisorb on transition metal surfaces with scission of the bond and the formation of M—X surface species. This dissociative type of chemisorption process is the invariant mode for hydrogen. Hydrogen chemisorption is reversible and the temperature required for the desorption of hydrogen as the hydrogen molecule is a function of the metal-hydrogen (surface) bond strength. For example, the desorption temperature (flash desorption maximum) is *ca.* 380 K for hydrogen on Ni(111)^[39]. Hydrogen chemisorption is an oxidative addition reaction in that there is a small but net electron transfer from the metal to the hydrogen atom to form a "hydride-like"^[42, 43] ligand. A measure of the electron transfer in a chemisorption reaction can be obtained by a relatively simple electrical measurement in which the *change* in the work function is determined; this is the change in work function on chemisorption referenced to the clean surface. This experiment is an important adjunct to the other analyses of the chemisorption process although the derived information obtained in this fashion is qualitative in character.

Hydrogen chemisorption on a metal is analogous to the reversible oxidative addition of hydrogen to low valent transition metal complexes as in eq. (1), where there is a formal oxidation of rhodium from Rh(I) to Rh(III) with the formation of the two σ Rh—H bonds^[44].



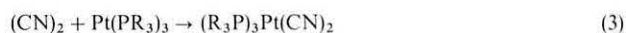
Analogous oxidative additions of halogens, oxygen, nitrogen and even carbon monoxide to some transition metal surfaces

are well established but generally these are irreversible, dissociative chemisorption processes. Among these diatomic molecules, an oxidative addition to a metal center in a coordination complex is known only for halogens [eq. (2)]. A dissociative



addition of O_2 , N_2 , or CO probably would require a minimum of two metal atoms. Hence this type of process may be found only, if at all, for nitrogen and carbon monoxide in additions to dinuclear metal complexes or to metal clusters.

Cyanogen appears to behave like hydrogen; it oxidatively adds to the surfaces of nickel group metals, reversibly in the case of Pt(110) and irreversibly in the case of Ni(111) where N_2 is thermally desorbed at high temperatures leaving carbon on and in the nickel crystal. As a check of the parallel between this metal surface chemistry and coordination chemistry, we have found that thermal decomposition of $\text{Ni}(\text{CN})_2$ yields N_2 and $(\text{CN})_2$ whereas $\text{Pt}(\text{CN})_2$ forms cyanogen^[4,5]. Oxidative additions of cyanogen to metal centers in zerovalent and low-valent coordination complexes are well established [see *e.g.* eq. (3)^[4,6]]. Thus, there is a qualitative parallel in the



chemical behavior of these metal surfaces and their coordination complexes for this cyanogen chemistry. Nevertheless, a major differentiation between metal surfaces and zerovalent metal complexes is evident in their reactions with nitrogen, and, in some cases (some metal surfaces), with carbon monoxide. Complexation without fragmentation prevails in coordination chemistry and dissociative chemisorption in surface chemistry. It is this very differentiation that is the basis of the relatively facile hydrogenation of nitrogen or carbon monoxide by some metal surfaces, *e.g.* iron. Conceivably, a highly unsaturated metal cluster might be capable of dissociating nitrogen, but such a reaction is relatively improbable. The analogy between metal surfaces and coordination complexes or clusters will be invalid or inapplicable in some chemical areas; the area of CO and N_2 chemistry is one of these *for the more reactive metals like iron*.

Displacement of dissociatively chemisorbed molecules like hydrogen and halogens by another molecule requires a surface recombination of the "radicals". Displacement of hydrogen in surface $\text{M}-\text{H}$ bonds or of halogen in surface $\text{M}-\text{Cl}$ bonds into the gas phase as H^{\bullet} or Cl^{\bullet} or as H^- or Cl^- is clearly an improbable event. In a thermodynamic sense, the probability of displacement of dissociatively chemisorbed halogen or oxygen by some molecule is low for most metals but displacement of dissociatively chemisorbed hydrogen, as the hydrogen *molecule*, by another molecule is a different matter. Since the temperature required for thermal desorption of hydrogen is not very high for most transition metals—the maximum in the flash desorption of hydrogen from nickel(111) is *ca.* 380 K—, displacement of dissociatively chemisorbed hydrogen would seem to be a distinct possibility, and parenthetically an important finding, as will be discussed in Section 5.3. To date, our limited exploratory studies have been negative^[3,9]. Exposure of a nickel crystal face(111), partially cov-

ered with hydrogen, to carbon monoxide did not seem to lead to desorption of hydrogen nor to a reduction in the flash desorption maximum for hydrogen. Perhaps the partially oxidized (through hydrogen oxidative addition) nickel surface so reduces the CO heat of chemisorption that a substantial weakening of the $\text{Ni}-\text{H}$ bond is not feasible^[3,9]. A stronger acceptor molecule then seems to be required. Donor molecules should increase the strength of the $\text{Ni}-\text{H}$ bond *if* in this sector the analogy to coordination chemistry is reasonably valid. Alternatively, the displacing molecule could be selected among the diatomic molecules that strongly and dissociatively chemisorb. Cyanogen, a *quasi* diatomic or halogen-like molecule in that the $\text{C}-\text{C}$ bond is weak and readily broken, could be an excellent molecule for hydrogen displacement from a surface. Iodine is a reasonable alternative to cyanogen but not a very practical one because of substantial contamination problems^[4,7]. In some of these interactions, there may be a chemical reaction rather than a simple displacement so as to yield HX rather than H_2 —in such a variation, the diagnostic value would be retained.

4.4. The Polymerizative Chemisorption Class

The antithesis of dissociative chemisorption is a molecular chemisorption whereby there is polymerization or oligomerization of many or several of the molecules. A possible example is the trimerization of acetylene to benzene. Because this type of chemisorption is not a first order process it is an unlikely event unless there is a high mobility of the molecules on the surface so that two or more molecules can approach and orient in such a fashion as to allow oligomerization to proceed. Polymerization initially at or on the surface and then out away from the surface (not totally on the surface) is however a well-established phenomenon in surface chemistry^[4,8].

Chemisorption of cyanogen on nickel(111) at 300 K does not give an ordered chemisorbed layer^[3,9]. However, warming to 400 K gives a very stable ordered (6×6) structure (see Fig. 12)^[3,9]. Because the $\text{C}-\text{C}$ bond energy in cyanogen, $\text{NC}-$

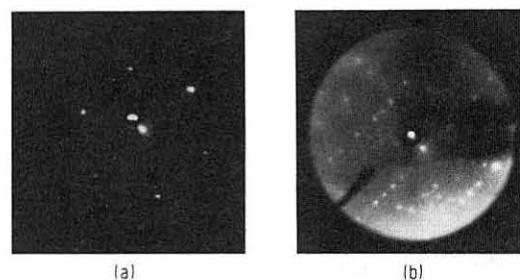
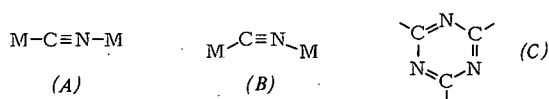


Fig. 12. a) Low energy electron diffraction pattern for a clean (111) face of nickel; b) (6×6) ordered pattern of cyanogen chemisorbed on this nickel face. The centered light spot with a dark halo is from the electron gun itself.

CN , is low and because CN is a strong field ligand in metal coordination chemistry, initial dissociative chemisorption is a highly probable event. Now CN could be normal or parallel to the metal surface. In binary low-valent transition metal cyanides, the cyanide ion is bonded to two metal ions in



a linear array (A). This geometry is not feasible on a flat (111) metal face but a bent array (B) is feasible and plausible. If a parallel orientation prevails for CN on Ni(111), mobility of the CN species on the surface could allow for a polymerization of the CN species to give a bound triazine derivative with the skeletal array (C). Two of these units could neatly fit into a (6 × 6) unit cell or to give a net similar to the layer nets observed in nickel group cyanides, *e.g.* Ni(CN)₂.

Polymerization of unsaturated organic molecules on coordination to a low-valent metal atom is established in coordination and organometallic chemistry. Trimerization of acetylenes to benzenes is a relatively common reaction and the trimerization of butadiene to 1,5,9-cyclododecatriene^[49] is known for zerovalent mononuclear nickel complexes.

5. Subclasses of Chemisorption on a Metal Surface

5.1. Subclasses of Associative Chemisorption: Extensive Rehybridization within the Molecule

Chemisorption of molecules that contain multiple bonds may involve an extensive rehybridization at the multiply bonded atoms. This possible type of chemisorption is appropriately considered with respect to the coordination chemistry for an acetylene molecule, RC≡CR. The simplest form of an acetylene chemisorption would be a σ-donor interaction of a π acetylene orbital and π-acceptor interaction of a π* acetylene orbital with surface metal atom orbitals^[50]. This would be fully analogous to the Dewar-Chat-Duncanson^[41] model of the ethylene-metal interaction (Fig. 11), and by analogy would yield a relatively weakly bound molecule which should be susceptible to facile displacement by other molecules such as carbon monoxide. However, acetylene compounds such as acetylene itself and 2-butyne, are very strongly bound on nickel(111)^[39], as an example of one well studied metal surface, and are not displaceable from the nickel surface by other molecules^[39].

There is an alternative binding of an acetylene if there are two or more adjacent metal atoms. Significant rehybridization of the acetylene carbon atoms may allow σ carbon-metal bonds, minimally two in number per acetylene carbon atom,

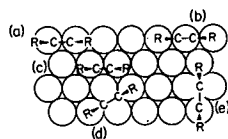


Fig. 13. Possible orientations (a—e) of a molecule RC≡CR on a close-packed metal surface ((111) face). All orientations other than the one centered on a single metal atom yield two or more metal-carbon bonds to the acetylenic carbon atoms.

to be formed (Fig. 13)^[51]. This type of acetylene binding is well documented in coordination chemistry for metal dinu-

clear and cluster complexes (Fig. 14)^[51,52]. Rather extensive studies of these polynuclear metal acetylene complexes have demonstrated a robust acetylene binding. Acetylene exchange reactions in these polynuclear complexes does not occur readily whereas such, exchange reactions are facile in mono-

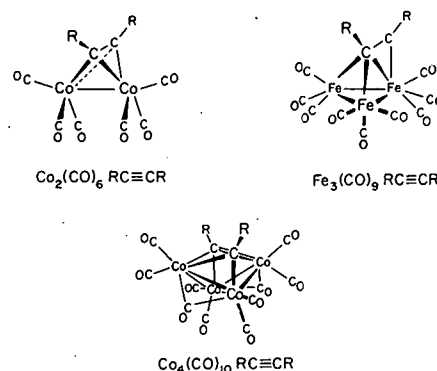


Fig. 14. Molecular structure of three classes of polynuclear metal-acetylene complexes (see discussions in references [51] and [52]). The bond length $d_{\text{C}\equiv\text{C}}$ in $\text{Co}_2(\text{CO})_6\text{RC}\equiv\text{CR}$ is 1.35 Å, in $\text{Fe}_3(\text{CO})_9\text{RC}\equiv\text{CR}$ 1.41 Å, and in $\text{Co}_4(\text{CO})_{10}\text{RC}\equiv\text{CR}$ 1.44 Å (mean values).

nuclear metal acetylene complexes (Fig. 11)^[52]. For example, diphenylacetylene exchange with di-*p*-tolylacetylene is extremely slow in the nickel-acetylene cluster complex, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_3$ at 300 K (reaction times of days). In the case of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2\text{C}_2\text{H}_2$ the exchange is detectable only at temperatures above 370 K^[52].

If the surface-coordination chemistry analogy is valid, an unsaturated molecule bound to a metal-surface through extensive σ-bonding of adjacent metal atoms to the (initially) unsaturated atoms, will not be subject to facile displacement by another molecule, at least at 300 K. The activation energy may be high for such displacements; in some cases, the activation energy may be greater than for alternative thermal reactions of the chemisorbed molecule. Possibly the displacement may be more readily effected with a molecule whose dissociative chemisorption raises the level of surface oxidation and decreases the binding energy of the initially bound molecule.

5.2. Subclasses of Associative Chemisorption: Molecular Rearrangement

A molecule may chemisorb on a metal surface without fragmentation (dissociation), but through a rearrangement of bonds within the molecule it may yield a chemisorbed species topologically disjoint from the original molecule. For example, an allene $\text{R}_2\text{C}=\text{C}=\text{CR}_2$ molecule may on chemisorption yield an acetylenic bound species ($\text{R}_3\text{CC}\equiv\text{CR}$). This possibility can be accurately probed by examining the chemisorption process for the individual isomers. We have exploited this chemical probe so as to demonstrate that CH_3CN and CH_3NC chemisorb as chemically and physically distinguishable isomers on the (111) face of platinum and nickel^[39].

All isomerization-based chemisorption processes are definable by a study of isomeric molecules and, if necessary, by isotopic labeling for an ultimate characterization by mass spectroscopic analysis of gaseous desorption products from a displacement reaction.

5.3. Subclass of Dissociative Chemisorption: Molecular Fragmentation in Hydrocarbons

The chemical feature that sharply distinguishes metal surface chemistry from known coordination chemistry, either that of mononuclear or polynuclear complexes, is the ease with which carbon-hydrogen bonds in organic molecules can be cleaved. Dehydrogenation of organic molecules is a thermodynamically and kinetically favorable process for clean metal surfaces, particularly under conditions whereby these reactions are effected in ultra-high vacuum chambers. This type of reaction is incisively documented for the chemisorption of ethylene on tungsten, where dehydrogenation occurs below 300 K to yield chemisorbed acetylene (or an isomer) and then C₂ (carbon) chemisorbed species are formed as the temperature is raised above 300 K^[53].

This potentially complex pattern of hydrocarbon chemisorption on a metal surface is of fundamental significance, especially in heterogeneous catalysis. For example, ethylene might chemisorb at 25°C to give (i) a molecular ethylene complex, (ii) vinyl (CH=CH₂) and hydride metal surface species, (iii) an acetylene and two hydride metal surface species, or (iv) a carbene or quasilallene species (CCH₂) and two metal hydride surface species. An example of the last possibility established in metal cluster chemistry is illustrated in Figure 15^[54].

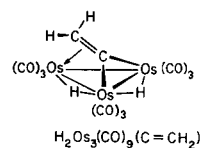


Fig. 15. Molecular structure of the cluster reaction product of ethylene and H₂Os₃(CO)₁₀ [54].

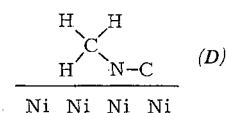
Actually, dissociative chemisorption of ethylene on metal surfaces is a relatively common surface phenomenon but the nature of the resultant chemisorbed hydrocarbon is not known.

Only one physical technique is available that will distinguish definitively between a molecular or an associative chemisorption and a dissociative chemisorption in which a molecular fragment or new molecule is generated by one or more carbon-hydrogen bond scissions per molecule. This technique, high resolution energy loss spectroscopy^[55], can discern the energy loss in inelastically scattered electrons associated with metal hydrogen bond vibrational excitations. At present this is not a routine technique and cannot be used with facility in general chemical studies of the chemisorbed state. Nevertheless, the four to six instruments, extant or under construction, could answer a number of key scientific questions in metal surface-hydrocarbon chemistry.

If M—H surface species could be displaced as hydrogen gas by a second molecule, then surface science would have a facile diagnostic chemical technique of tremendous general import. One practical problem in accurately assessing hydrogen desorption through a displacement reaction is that when a molecule with any capacity to chemisorb on metals is introduced into the chamber there will be a momentary increase in the hydrogen background—typically, most of this is not associated with desorption from the single crystal of metal but rather from chamber walls or a bit of ion pump indigestion which literally throws hydrogen gas back into the chamber.

An isolation cell and cryogenic pumping can minimize this problem; the elegant solution is a molecular beam displacement experiment. Development of such a diagnostic chemical probe is a major objective of our research.

Methyl isocyanide is strongly chemisorbed on the (111) face of nickel^[39]. Initial chemisorption probably involves a bonding interaction of the carbon and nitrogen atoms of the isocyanide with several nickel atoms; there is a precedent for such a bonding interaction in a nickel isocyanide cluster molecule, Ni₄[CNC(CH₃)₃]₇^[55]. In this case, the C—N axis would be above and more or less parallel to the nickel surface as in (D) and this then places the hydrogen atoms of the



methyl group proximal to the surface. In coordination chemistry, the close approach of a ligand hydrogen atom to a coordinately unsaturated metal atom can lead to an oxidative addition of the C—H bond^[56, 57]. Hence, oxidative addition of a C—H bond to a proximal nickel atom in the methyl isocyanide case should be a relatively favorable process.

CH₃NC is irreversibly chemisorbed on nickel and is not susceptible to displacement by other molecules. With flash heating, hydrogen is desorbed at several temperatures, the lowest of which is 380 K, the characteristic desorption temperature for hydrogen^[39]. If the crystal with chemisorbed CH₃NC is annealed at ca. 350 K before flash heating, no hydrogen is desorbed at 380 K, though hydrogen desorption does occur at elevated temperatures^[39]. These thermal desorption experiments suggest that CH₃NC on chemisorption undergoes a further reaction, a dehydrogenation, either at 300 K or slightly above. Dehydrogenation reactions of ligands are not as common in coordination chemistry as on metal surfaces but they are well documented for low valent and coordinately unsaturated complexes in which a ligand hydrogen atom is in close proximity to the metal atom^[56, 57]. Several examples are illustrated in Figure 16.

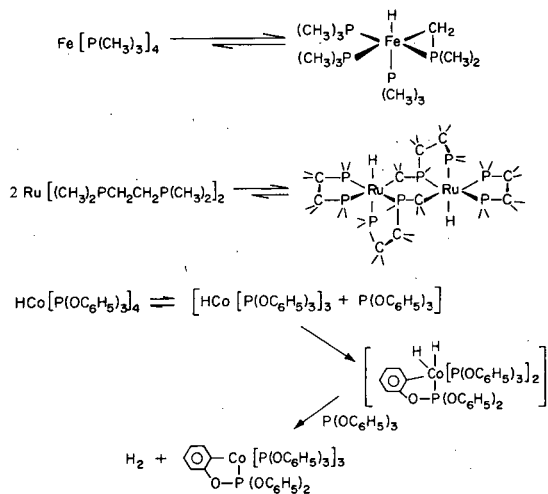


Fig. 16. Examples of molecular metal complexes in which an intramolecular C—H bond addition across the metal center has occurred to yield a metal-carbon and a metal-hydrogen bond. (For a more complete discussion, see the reviews by Parshall [56] and by Webster [57].)

Any chemisorption of an unsaturated hydrocarbon or hydrocarbon derivative that places carbon-hydrogen bonds close to surface metal atoms is apt to be accompanied by a cleavage of these carbon-hydrogen bonds. In the acetonitrile chemisorption on nickel, the perpendicular alignment of the nitrile places the carbon-hydrogen bonds of the methyl group sufficiently distant from the surface nickel atoms that C—H bond scission does not substantially occur on chemisorption at 300 K. On the other hand, olefins and acetylene should chemisorb initially with the unsaturated carbon-carbon bond more or less parallel to the metal surface thereby orienting substituent atoms near the metal surface. In these cases, carbon-hydrogen bond cleavage is a probable process near or slightly above room temperature at least for the more active metals. Aromatic hydrocarbons should exhibit a similar behavior. Low energy electron diffraction data for benzene chemisorbed on platinum are available but an intensity analysis has not been made^[58]. The unit cell size is such that several models would appear to be possible. One possible model has a bound dehydrobenzene molecule formed by a dehydrogenation reaction. This dehydrobenzene species could be bound to the platinum surface through two σ Pt—C bonds and then, by tilting of the ring away from the normal, further bound through a π bond with additional surface metal orbitals. Interestingly, there is a model for this suggested chemisorbed state of benzene in molecular metal cluster chemistry. Benzene reacts with $\text{Os}_3(\text{CO})_{12}$ at ca. 473 K to form a dehydrobenzene complex which presumably^[59] has the structure shown in Figure 17.

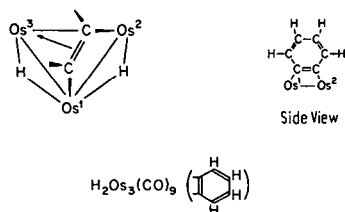


Fig. 17. Structure postulated for the reaction product from $\text{Os}_3(\text{CO})_{12}$, or better $\text{H}_2\text{Os}_3(\text{CO})_{10}$, and benzene [59]. An X-ray crystallographic study is required for confirmation of this postulate. A precise determination of C—C bond separations in the six-membered ring may provide a better indication of the nature of the bonding between the ring carbon atoms and the unique osmium atom.

One intriguing chemical possibility for modification of a dissociative (C—H bond scission) chemisorption of an olefin, an acetylene, or an aromatic hydrocarbon would be to presaturate the surface with hydrogen before chemisorption of the hydrocarbon—this might inhibit or even totally block carbon-hydrogen bond scission in the bound hydrocarbon.

6. A Model for Hydrogen Atom Mobility in Hydrocarbons

A general feature of surface chemistry is the hydrogen atom lability in hydrocarbon species chemisorbed on metal surfaces; H—D exchange is generally a facile process in C_xH_y — C_xD_y or C_xH_y — D_2 mixtures. Recently, *Shapley et al.*^[60] showed that a methyl derivative of an osmium cluster is in a facile equilibrium with a methylene-hydride cluster derivative (Fig. 18). This discovery in metal cluster chemistry provides a possible model for the nearly pervasive phenomenon of hydrogen atom lability in chemisorbed hydrocarbon species.

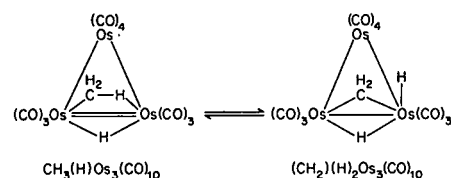


Fig. 18. The structures [60] of the equilibrium solution species of composition $\text{Os}_3(\text{CO})_{10}\text{CH}_4$ [60]. The methylene structure has been defined by an X-ray crystallographic analysis of a single crystal of this isomer. Although the precise structure of the methyl derivative is yet to be defined for the crystalline state, the spectroscopic data suggest that the methyl group is in an unsymmetric bridging position.

7. Orientational Effects

The obvious critique of the high vacuum, single crystal surface technique is that a single crystal face hardly emulates a metal film or highly dispersed metal particles. The point is granted. However, a careful assay of the chemistry of a given metal requires a systematic investigation of the key crystal face chemistry for the metal in question. Crystal face chemistry can be demonstrably diverse. For example, the platinum (110) surface reversibly chemisorbs cyanogen in a relatively strong fashion yet the (111) face of platinum reversibly interacts with cyanogen to a very minor extent. Thus, the details of single crystal metal chemistry can delineate, in principle, the essential bonding or geometric details of the chemisorption process. *Somorjai et al.*^[19] have demonstrated the difference in reactivity of surface metal atoms that lie in different environments, e.g. the atoms in the terraces, steps and kinks of high Miller index faces which come closer to real surfaces than do low index or "flat" crystal faces.

The metal-metal coordination number for individual surface metal atoms is markedly affected by the nature of the crystal face. In the terrace or flat section of a (111) face of a face-centered cubic metal, the coordination number is nine—if there is a break, a step, in this terrace, the metal atom at the top of the riser has a coordination number of seven—if the step is irregular so as to generate a kink, the leading atom of a kink has a coordination number of six (Fig. 1). Adatoms on a terrace have coordination numbers of three, four and five for a single, a pair and a triad of adatoms, respectively.

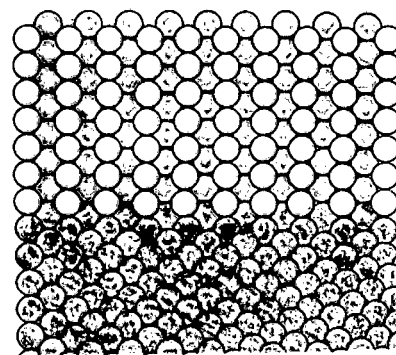


Fig. 19. A representation of the (110) face-centered cubic structure. The representation is generated from the (111) face (dark shaded lower region) and clearly shows the ordered step-like character of this low Miller index face, a face of relatively low thermodynamic stability which often undergoes reconstruction under the conditions of a chemisorption process.

A (110) face of a face-centered cubic metal is like a stepped surface (Fig. 19 and 20) and the "protruding" atoms have a coordination number of only seven. We would expect to a first approximation that site reactivity of surface metal atoms

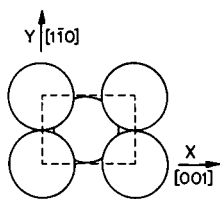


Fig. 20. The unit cell for the (110) face of a face-centered cubic crystal. Coordination number for the top four atoms is only seven whereas it increases to eleven for the partially covered central metal atom.

will rise sharply with the decrease in the metal-metal coordination chemistry as observed for molecular coordination compounds. The initial studies of Somorjai are consistent with this speculation; it will be of great importance to test this hypothesis in general systematic chemical studies of metal crystal face chemistry.

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- [7] In the final analysis, there is a visual comparison of the experimental curve with the theoretical curves for postulated models. If carried out systematically, this analysis gives a complete picture for atoms chemisorbed on the surface. Comprehensive analysis of the chemisorption state of a molecule on a surface is at best difficult because a molecule may chemisorb, with the topological or graphical features of the molecule intact, with rearrangement, with polymerization, or with scission of one or more bonds. As was true in the early days of electron diffraction of gaseous molecules, chemical intuition is a most important element in the study of molecules chemisorbed on surfaces.
- [8] A comprehensive enumeration of low energy electron diffraction studies has been presented by Tong [2]. The especially notable studies of atoms chemisorbed on a metal surface initiated by T. N. Rhodin *et al.* (Cornell University) and by S. Andersson *et al.* (Chalmers Institute of Technology) set the stage for the theoretical development of the analysis by Duke, Pendry, Jepsen and Marcus. See the application by J. E. Demuth, D. W. Jepsen and P. M. Marcus, *Phys. Rev. Lett.* 31, 540 (1973) and 32, 1182 (1974) for the overlayer structures of O, S, Se and Te atoms on Ni(100), Ni(111) and Ni(110).
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- [21] In some instances, there is no significant kinetic or thermodynamic differentiation between the high vacuum and the atmospheric or super atmospheric reactions, as in the CO+O₂ reaction (D. R. Monroe, Ph. D. Thesis, University of California, Berkeley 1972). For other reactions, the thermodynamic parameters change markedly with pressure. Most critically, a pure metal surface is often not representative of the so-called metal catalysts where oxide phases and carbon overlayers are often the dominant surface phases.
- [22] In surface science, the terms associative or dissociative refer explicitly to chemisorption processes of molecules that occur, respectively, with no fragmentation or with fragmentation of the molecule. In coordination chemistry, the term dissociative or associative reaction has a reaction mechanistic connotation. A dissociative reaction follows a step sequence
- $$ML_x \rightleftharpoons ML_{x-1} + L \text{ and } L' + ML_{x-1} \rightleftharpoons ML_{x-1}L'$$
- whereas associative follows the sequence
- $$ML_x + L' \rightleftharpoons ML_xL' \text{ and } ML_xL' \rightleftharpoons ML_{x-1}L' + L$$
- (See C. H. Langford, H. B. Gray: *Ligand Substitution Reactions*. Benjamin, New York 1966, Chap. 1.) Since reactions of molecules with a metal surface will almost invariably be associative in a reaction mechanistic context, the less compact terminology of molecular associative and molecular dissociative chemisorption is now recommended to avoid any confusion by scientists from different disciplines. New chemisorption terminology such as fragmented and intact, although more concise, might be less readily accepted by the surface science community because the present terms are of long standing usage.
- [23] The desired crystal may be cut from a larger crystal by an electric arc or a diamond saw or alternatively may be purchased to specification.
- [24] Diameter and thickness will vary substantially in practice depending upon the nature of the physical and chemical studies.
- [25] With care, this percentage figure can be raised to 80–90%.

- [26] This is not a standard or preferred mounting procedure but merely an example.
- [27] The metal sample may also be heated indirectly by electron bombardment of a shielded metal cup as shown in Figure 2.
- [28] Full characterization details for surface states are critical elements in scientific publications. Cleaning procedures should also be presented for further insight into the research and for assistance to others not familiar with the particular metal in question.
- [29] The grazing incidence experiment has the advantage of greater sensitivity. With the cylindrical mirror analyzer which is of the window filter type, a maximal signal-to-noise ratio can be realized. With a cylindrical mirror analyzer, the Auger analysis can be achieved in a very short time, 10^{-2} seconds, compared to times of about one minute for the retarding grid analyzer—thus, potential electron beam damage to the surface species can be minimized. This method of Auger electron analysis is the method of choice if line shape information is desired.
- [30] A careful analysis of standards can raise the level of the Auger analysis to a substantial degree. In addition, the line shape of the Auger peaks can, in principle, provide details of the structural and electronic states of the chemisorbed states. Careful comparative studies of the isolated gas phase spectra of molecules with their spectra on chemisorption on surfaces may provide information about intimate features of the chemisorbed states; see *J. M. White, R. R. Rye, J. E. Houston*, *Chem. Phys. Lett.* **46**, 146 (1977).
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