Role of surface bonding on liquid-crystal alignment at metal surfaces

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The alignment of a nematic liquid crystal, 4′-*n*-pentyl-4-cyanobiphenyl (5CB), on several smooth metal (Cr, Cu, Ag, and Au) surfaces was observed experimentally. Perpendicular (homeotropic) induced alignment was observed for Cu and Ag boundary layers, whereas parallel alignment was observed for Cr and Au. These differences are discussed in relation to the differences in chemical bonding interactions at the surfaces as described by theoretical calculations performed for the cases of Cu, Cr, and Au. Several differences in orbital interactions, as well as a sensitivity to bonding configurations, are illustrated with the aid of extended Hückel calculations on hypothetical organometallic complexes and extended-Hückel–tight-binding calculations of the interface for parallel versus perpendicular adsorbate orientations.

I. INTRODUCTION

Since 1970, studies of liquid-crystal (LC) surface interactions and alignment have proceeded actively, and several reliable methods of producing structurally inhomogeneous surfaces have been found that are effective in controlling the alignment and orientation of a LC at solid surfaces.[1] Recent studies have shown that variable oblique alignment of a nematic liquid crystal (NLC) can be achieved by the interaction of NLC's, with compositionally and microscopically inhomogeneous but macroscopically homogeneous surfaces.[2,3] However, in spite of the great effort being devoted to the study of alignment of LC's, the molecular interactions with, and alignment by surfaces, remain among the least understood areas of LC physics and chemistry.

The interaction between the LC molecules and the surface could induce orientational order and, hence, affect bulk-alignment properties of LC cells. Because alignment schemes usually involve roughening of the surface, it is difficult to separate the geometrical effects due to roughness from bonding interaction effects. In this paper, we will address the role of surface-bonding interactions on the alignment properties in the bulk phase by comparative studies of the induced alignment for a NLC, 4′-*n*-pentyl-4-cyanobiphenyl (5CB, also referred to as PCB and K15) bordered by various flat metal surfaces from both experimental (measurements were made for Cr, Cu, Ag, and Au surfaces) and theoretical (computations were performed for Cr, Cu, and Au) approaches. The results show that chemical bonding is an important factor in the LC's surface alignment.

Figure 1 shows two proposed bonding configurations of a single 5CB molecule on a flat metal surface (for simplicity, the axis of the molecule has been chosen to lie entirely along the parallel or vertical directions, in each case). In order to gain insight on the chemical origins of preferred surface anchoring configurations, molecular-orbital calculations were performed on hypothetical organometallic complexes consisting of a fragment of the 5CB, cyanobenzene, interacting with isolated metal atoms at several bonding locations. Surface anchoring resulting from chemical bonding considerations would most likely involve the 4-cyano-biphenyl moiety of the

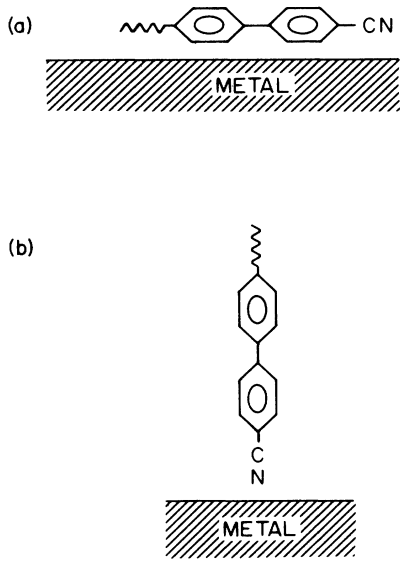

FIG. 1. Schematic view of a 5CB molecule oriented (a) parallel and (b) perpendicular to the surface of the metal substrate.

5CB molecule, and the hydrocarbon tail is approximated as a noninteracting entity. This is a reasonable approximation, since chromium forms metallocenes such as dibenzenechromium,[4] Cu, Au, and Ag, form cyanide complexes,[5] and the alkyl chain is weakly interacting by comparison. For computational simplicity, the cyanobenzene fragment was used to illustrate the basic bonding features of the full 5CB molecule for each case.

These complexes involving a single metal atom interacting with cyanobenzene are not intended to approximate the chemical bonding activity at a surface. Rather, they form a starting point, from which we can visualize the electronic interactions that drive the actual surface bonding. A more realistic model may be achieved by performing calculations involving a cluster of metal atoms[6] or by extension of the interface to two dimensions by applying periodic boudary conditions. The latter approach was chosen, and was implemented using the extended-Hückel–tight-binding method[7] for a layer of cyanobenzene upon a two-layer slab of metal. To simplify the calculations, intermolecular interactions were neglected by considering a dilute overlayer. The effects of surface contaminants on the metal films have also been neglected for these studies.

In this paper we will present the experimental results, discuss the computational results for the molecular-orbital calculations, and summarize the main features of the two-dimensional, interface calculations. The simplified molecular-orbital calculations served as a guide to chose the possible bonding geometries for the interface calculations. Because their interpretation is simple, the molecular-orbital calculations serve to illustrate the main features of bonding for the case of Cr, where surface band-structure effects were found to be less important than the cases of Cu and Au. For the case of Cu, the molecular-orbital calculations predict the correct results, and the results of the slab calculations are used to display the subtleties of the metal-surface interactions with the cyanobenzene. Although Au might be expected to behave similarly to Cu, both the experimental and theoretical findings agree that there are major differences between the Cu and Au interactions. For Au, metal-metal hybridization features play a deciding role, and the results of the two-dimensional surface treatment are used to explain the behavior. In Sec. II we first discuss the experimental measurement methods and results. A section on the computational methods follows. Finally, the computational results are discussed in detail in Sec. IV.

II. EXPERIMENTAL METHODS AND RESULTS

Different experimental methods have been used to study the surface induced orientational ordering, such as the induced birefringence,[8,9] conoscopy method,[8] magnetinull method,[10] transmission ellipsometric techniques,[11,12] evanescent wave-ellipsometric techniques,[13] and optical second-harmonic generation.[14] In this study we are interested in determining the induced orientational ordering in liquid crystals by smooth metal surfaces. The orientational ordering is either parallel to the surface (which we refer to as parallel orientation) or vertical to the surface (homeotropic orientation, which we refer to as vertical orientation). Therefore, we use the induced birefringence method with verification for consistency by the conoscopy method.

The construction of the samples is illustrated in Fig. 2. The flat metal films of Cr, Cu, Ag, and Au with thickness of about 1000 Å were either sputtered or evaporated onto Cr-coated silicon wafers.[15,16] For Cr and Au, both sputtering and evaporation methods were used in the experiments, and for Ag and Cu, evaporated films were used. Both methods were found to produce the same LC alignment for the samples tested. In the evaporation experiment, the metals were thermally evaporated from a tungsten (for Cr, Cu, and Au) or a tantalum (for Ag) boat in a medium high vacuum with a pressure between 4×10^{-6} and 1×10^{-6} Torr. The sputtered films were formed by dc argon sputtering of the metal targets onto rotating targets, producing highly uniform coatings. The chamber has a base pressure of $\sim10^{-7}$ Torr. Typical sputtering conditions were ~1 A ion current at ~450 V with an argon pressure of $\sim7\times10^{-4}$ Torr. In our experiments, sputtered and evaporated films produce equal quality continuous metal films having high reflectively, uniformity [featureless under Scanning electron microscope (SEM) investigation], and are mirror like in finish.

The top cover glass surfaces were coated with silane *N,N*-dimethyl-*N*-octadecyl-3-aminopryltrimethoxysilyl chloride (DMOAP),[17] using the procedure described in Ref. 3, which aligns the LC vertically to the surface,[1,18] and were offset from the metal surface by spacers of thickness of about 12 μm. The 5CB was injected into the cells by capillary flow at about 50 °C. The major component of the surface alignment ("vertical" or "parallel") was determined by observing the sample in a microscope between cross polarizers in the reflection mode and checking for the presence or absence of birefringence. Birefringence is absent for the case of vertical alignment, whereas birefringence is induced for parallel alignment. The parallel alignment is further verified by checking the disclination line.[8] We have also obtained consistent alignment results using the conoscopy image for transparent glass substrates coated with the metal of a thickness less than 100 Å.

Using the three experimental methods described above, we have found that for the nematic 5CB, Ag and Cu produce vertical orientation, whereas Au and Cr produce parallel orientation. Although these experiments have been performed using thick (~1000 Å) continuous metal films, the results are also in agreement with the respective

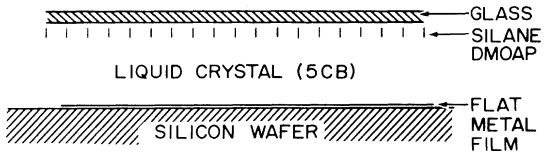

FIG. 2. Configuration of the cell used for observation of the liquid-crystal-induced orientational ordering.

result for Cr, Cu, Ag, and Au with a thickness of less than 100 Å, for which randomly distributed microscopic metal islands are formed.[3]

The experiments were performed at room temperature. In general, except near the vicinity of the phase transition temperature, the parallel or vertical LC alignment does not depend on temperature.[1] We also performed the alignment experiment using thermally evaporated films with the four metals on different LC materials, such as 4-cyano-4′ hexylbiphenyl (6CB, also referred to as K18), E7 (an E. M. Merck nematic mixture) and *N*-(*p*-methoxybenzylidene-*p*-butylaniline) (MBBA). The same alignment results as those of 5CB are obtained. These results are in agreement with that reported in Ref. 3.

III. COMPUTATIONAL METHODS

The semiempirical, extended-Hückel linear-combination of atomic orbital method[19,20] was applied, for hypothetical organometallic compounds consisting of two types of configurations of a single-metal-atom interaction with cyanobenzene, a fragment of the 5CB. As shown in Fig. 3, two types of bonding configurations were considered. Figure 3(a) shows the metal atom placed above the benzene ring of the cyanobenzene, and Fig. 3(b) shows the metal atom bonded with the cyano group. The carbon-ring bond angles and bond distances taken were those of benzene (C—C, 1.39 Å) and (C—H, 1.1 Å), the cyanide C—N distance was taken to be 1.15 Å, and the cyanide-to-benzene ring distance was chosen to be 1.5 Å. The placement of the metal atom above the benzene ring in Fig. 3(a) was chosen to be 1.6 Å, the distance between the Cr atom and arene ring in dibenzenechromium.[4] The existence of a local minimum for Cr placed above the benzene ring in several arene complexes was verified by Rossi[21] using *ab initio* calculations. Three metal-to-nitrogen bond distances were compared for consistency (1.7, 1.85, and 2.1 Å). Slater-type orbitals were used, with two exponential terms for the 3*d* orbitals (for Cr and Cu) and 5*d* (for Au) orbitals. The exponents obtained by Clementi[22] for the Cr 3*d* orbitals were used, and the coefficients and remaining parameters were taken from the charge iterated values used by Rossi[23] for a chromium $3d\pi$ complex with a polyimide fragment.[24] The parameters for Cu were obtained from Elian *et al.*[25] and the values for Au from Komiya *et al.*[26] were used.

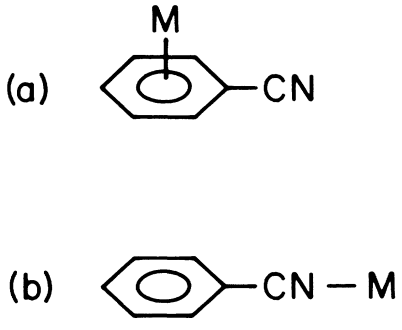

FIG. 3. Two configurations used for molecular-orbital calculations. (a) Metal atom bonded above the phenyl ring of the cyanobenzene and (b) bonded to the nitrogen of the cyano group.

The interface calculation utilized the extended-Hückel–tight-binding method for a two-layer slab of metal and one adsorbed layer of cyanobenzene. The (111) surfaces of Au and Cu, and the (110) surface of Cr were chosen, which are the lowest energy surfaces, in each case. For each surface, two bonding configurations for perpendicular alignment were considered, bonding of the nitrogen of the cyano group directly on top of a metal atom, and at a site bridging two metal atoms. The configuration chosen for the parallel orientation positions a metal atom directly below the phenyl ring, analogous to the metallocene complexes. The chosen orientations cover the most likely bonding interactions, but are not meant to be exhaustive. Dilute overlayers were used for the computations. Therefore, hybridization of the metal atoms of the surface is considered, but the adsorbate-adsorbate interactions are not included in this study. For Cu and Au (fcc), the unit cell contained 16 metal atoms and one cyanobenzene molecule. For Cr (bcc), the unit cell contained 15 metal atoms and one molecule. The key results of the slab calculations will be discussed in the following sections to augment the molecular-orbital computations and to allow full interpretation of the experimental results, and the computational details for the extended interface calculations are described in a separate publication.[27]

IV. COMPUTATIONAL RESULTS AND DISCUSSION

The first consideration is a description of the orbital composition and symmetries of cyanobenzene. The construction of the molecular orbitals for cyanobenzene from the fragment orbitals of CN and benzene is shown in the interaction diagram in Fig. 4. The orbitals of cyanobenzene (center) are formed by combining the molecular orbitals of the fragments, CN (left) and benzene (right). The degeneracy of the e_{1g} orbitals of benzene (D_{6h} symmetry) is formally removed by the reduction of the symmetry to C_{2v} to form the a_2 and b_2 orbitals of cyanobenzene. The a_2 and b_2 levels in the central panel in Fig. 4 are nonbonding with respect to the CN fragment; they remain essentially unchanged upon combination of the cyanide and benzene fragments. The a_1 orbital of benzene, which is formed from *p* orbitals which lie in the plane of the ring, interacts with the uppermost, filled σ orbital of CN to form the a_1 orbital of cyanobenzene (shown). The E_{2u} antibonding orbitals of benzene split upon combining with the π^* orbital of CN to form the a_2 and b_2 antibonding orbitals of cyanobenzene. The b_2 level is lowered, whereas the a_2 level is not significantly affected. The b_2 level is important because it becomes the characteristic acceptor level of this molecule.

Differences in chemical bonding, and consequently, the LC surface alignment properties, are derived from the differences in the electronic structure of the contrasting surfaces. Contrasting the chemical bonding that occurs

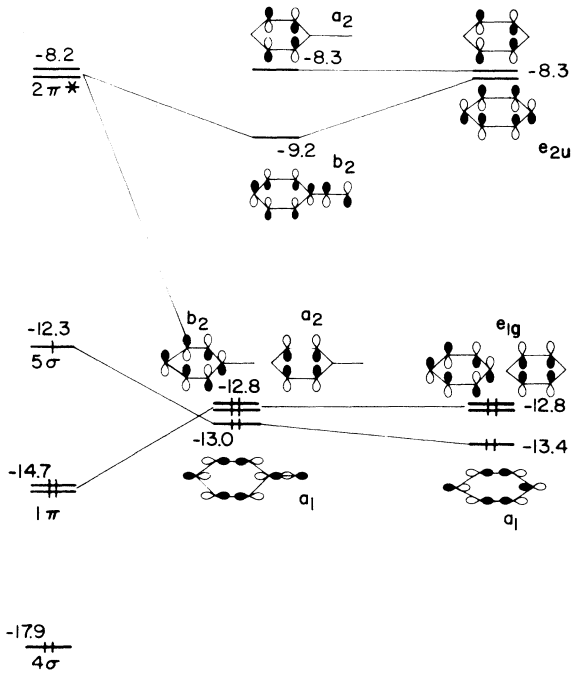

FIG. 4. Interaction diagram showing the orbitals of cyanobenzene (center) and their origins from the orbitals of cyanide (left) and benzene (right).

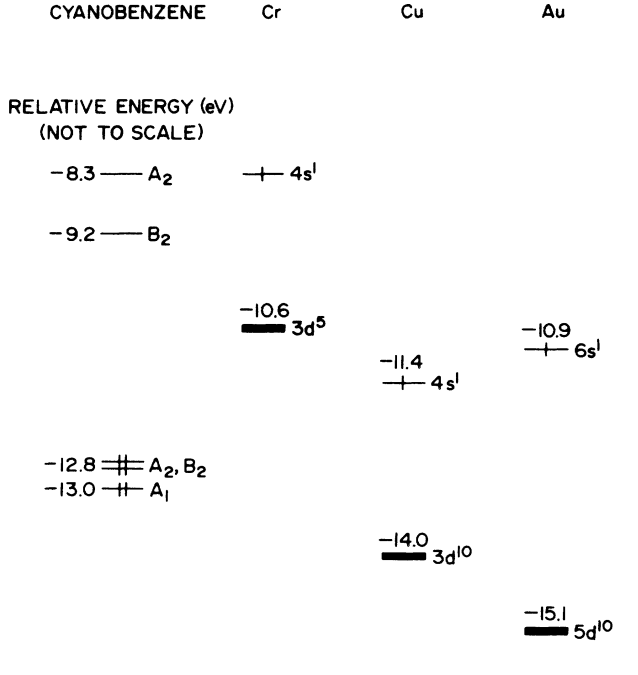

FIG. 5. Relative energy levels of frontier orbitals of cyanobenzene (left) and the *d* and *s* orbitals of the metal atoms.

for the bonding of single metal atoms (comparing the metals) at different locations is a useful exercise, which gives insight into the surface interactions occurring in the actual experiment, while the differences due to the extended structure of the surface are revealed in the slab calculations. The molecular-orbital calculation predicts the correct alignment for Cr (parallel) and Cu (perpendicular). For Au, parallel alignment is observed, whereas the vertical alignment is favored by the molecular-orbital calculation and the parallel configuration is correctly predicted when the surface electronic wave functions are utilized in the slab calculation.

We first discuss the results of the molecular-orbital calculation for Cr, with the aid of an interaction diagram, to illustrate the main features of the surface bonding interactions. The extent of bonding that occurs between the symmetry-related orbitals for a given configuration depends on both the overlap of the respective wave functions and the corresponding energy-level separation. Figure 5 compares the relative energy levels of cyanobenzene with the relative ionization energies of the *s* and *d* atomic orbitals of Cr, Cu, and Au. Also indicated in Fig. 5 are the populations of the implicated orbitals. Usually, it is the frontier states which are implicated in the reactivity. For Cr, the frontier level of cyanobenzene is within the *d* block, whereas the *d* blocks of Cu and Au are removed to an energy below the frontier orbitals. For the case of a Cr atom interaction with cyanobenzene, it was observed that placement above the aromatic ring was energetically preferred over the cyanobenzene bonding location. This geometry results in an interaction similar to that observed in dibenzenechromium and in Cr interaction with polyimide model compounds.[24] Figure 6 shows a partial interaction diagram for the case of Cr bonding at the benzene ring. The two lowest-lying unoccupied orbitals (a_2 and b_2) of cyanobenzene combine with the occupied d_{xy} and $d_{x^2-y^2}$ levels of Cr to form bonding (shown) and antibonding levels (not shown). The energy levels shown are the relative levels which result from the extended-Hückel calculation. By comparison, the case of Cr bonded to the nitrogen of cyanobenzene was found to be essentially noninteracting. The total-energy difference for the two configurations was ~ 3 eV, favoring the π-bonded configuration. It is noted that the total energies obtained from the extended-Hückel method originate from orbital overlap and, therefore, the trends of the relative energies for comparative complexes, rather than absolute energies, are observed in these studies. The strong differences in bonding for the two configurations lead us to believe that a π-bonding interaction of the 5CB involving the surface *d* band may be the driving force of the experimentally observed parallel induced alignment. The two-dimensional interface calculation also shows preference for the π-bonded configuration. The *d* band of the Cr surface is responsible for this interaction, with the a_2 and b_2 levels of cyanobenzene each being lowered by ~ 0.4 eV due to bonding. By comparison, the perpendicular bonding configuration shows little bonding effect. For this example, the molecular complex picture was representative of the surface bonding because the Cr surface interaction is driven by the *d* band of the Cr and, therefore, shows some of the character of the $3d$ π bonding observed for the hypothetical complex. For Cu, the surface band character of the metal reveals effects due to metal hybridization

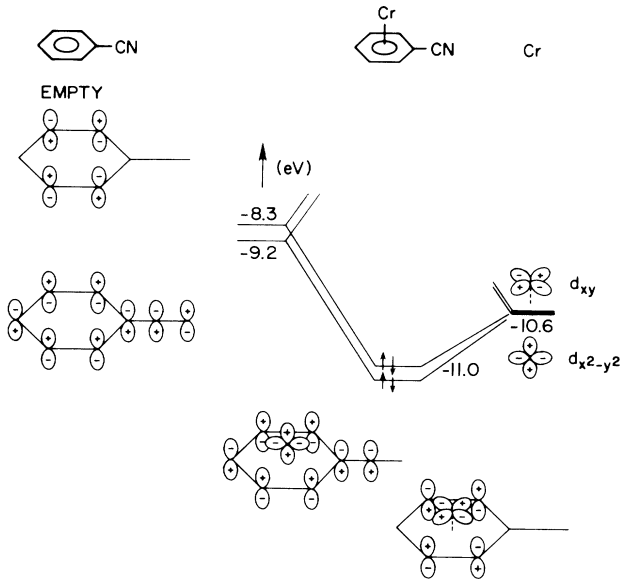

FIG. 6. Interaction diagram for a Cr arene complex with cyanobenzene.

at the surface. For Au, effects which depend on the surface hybridization are dominant.

The molecular-orbital calculations for Cu indicate a strong preference, of ~ 1.5 eV, for bonding of the Cu atom to the CN group compared to bonding above the phenyl ring, in agreement with the experimental result. Again, we note that we utilize the relative, but not the absolute energy information from the extended-Hückel calculations. The relative energy levels of Cu and Cr with respect to cyanobenzene are shown in Fig. 5. The d orbitals of Cu are filled and are lower in energy than the half-filled d orbitals of Cr. Because of this difference in relative energies of the metal atomic orbitals, the metal $3d$ interaction with the antibonding orbitals of cyanobenzene which was observed for Cr is not energetically favorable for the Cu atom. Instead, mixing of the Cu atomic orbitals with the filled levels of cyanobenzene can occur when the Cu atom is placed at the CN site. The a_1 level of cyanobenzene which lies at ~ -13.0 eV was found to interact with the d_{z^2} metal atomic level. Other interactions occur involving bonding orbitals which are lower in energy (-14.2 eV). However, the aforementioned σ-bonding interaction is strongest and is preserved in the slab calculation.

Inclusion of metal surface interactions in the slab calculation also shows the preference for vertical alignment of the cyanobenzene molecule with respect to the Cu surface, and further illustrates some of the metal hybridization features which come into effect. The slab calculations show the a_1 orbital of cyanobenzene is involved in a donor interaction with a mixture of Cu d, s, and p states (acceptor states). A charge transfer, or "back-bonding" interaction between filled-metal d states of the copper and the b_2 level is also now observed. The relative energies of the b_2 and copper d states are critical for this interaction. The copper atomic d levels are at a low energy relative to the b_2 state of cyanobenzene. Hybridization of the metal states provides states which are energetically compatible for interaction with the b_2 molecular orbital by raising the Fermi energy of the surface.

The slab calculations for Au show a broader bandwidth for Au, compared to Cu. This originates largely from the spatially diffuse character of the Au orbitals, which lead to increased orbital overlap. In this case, the metal-adsorbate interaction is weak compared to the metal-metal interaction, resulting in competing interactions which influence the overall bonding geometries. This is contrasted to the case of the Cr surface interaction with cyanobenzene, in which the adsorbate interaction with the metal is strong. The molecular-orbital calculations for the Au atomic interaction shows similarities to Cu in the CN-bonded case and similarities to Cr in the π-bonded configuration. Due to the metal hybridization for the configuration of the extended surface, and the corresponding broadening of the surface bands, the reactivity of the surface with respect to the adsorbate interactions is altered with respect to the single-atom case. The interaction which dominates, in the slab calculation, is a charge transfer interaction from the hybridized metal states into the a_2 and b_2 unoccupied levels of the cyanobenzene, which parallels the example of Cr, but with the corresponding surface electronic states for Au. It is noted that the molecular-orbital calculation of the single-metal atom organometallic complex results in a reversal of the favored interactions, due to the depth of the d levels of Au. The Fermi level is raised by the surface hybridization, the bands are broadened, and the π-bonding interaction becomes energetically favorable.

We have illustrated, by using the example of 5CB interaction with contrasting metals, that chemical bonding effects play a deciding role on the alignment of liquid crystals. The experimental cells were made on optical quality flat metal surfaces to reduce possible effects due to roughness, and a reasonable approximation for the 5CB molecule was made by considering the interactions of the cyanobenzene moiety. The latter, fragment approximation is justified because the CN and phenyl groups are the moieties which are expected to be chemically active. For the case of a weak interaction of the phenyl group with the surface, such as in the case of Au, the alkyl chain is important, but would not change the parallel alignment. Effects due to in-plane orientation have also been observed,[27] but do not change the basic alignment (parallel versus vertical).

Bonding interactions at Cr, Cu, and Au surfaces were compared. The example of cyanobenzene interaction with Cr was illustrated with the pictorial aid of an interaction diagram derived from a molecular-orbital calculation on a related organometallic complex. For Cr, parallel alignment arises from a charge transfer interaction involving a Cr d electron interaction with unfilled orbitals of the cyanobenzene when Cr is allowed to interact with the benzene ring of the molecule. The vertical alignment for the case of Cu is explained by bonding of the Cu to the CN group via the a_1 filled orbital of the cyanobenzene molecule, which is a donor interaction, and a back-

bonding, or charge transfer interaction, between the metal hybrid states and the b_2 unoccupied level of the cyanobenzene. For Au, a charge transfer interaction similar to that of Cr occurs, from the hybrid metal states into the a_2 and b_2 unoccupied levels of the adsorbate bands.

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