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STRUCTURE DETERMINATION OF MOLECULAR ADSORBATES WITH DYNAMICAL LEED AND HREELS

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Abstract

Molecular adsorbate structures can be determined by combining Low-Energy Electron Diffraction (LEED) with High-Resolution Electron Energy Loss Spectroscopy (HREELS). The HREEL vibrational spectroscopy identifies the molecular species, whose bond lengths and angles are obtained by LEED. Appropriate calculational methods are required in LEED to solve complex molecular structures: such methods will be discussed for large molecules, for large unit cells and for disordered adsorbates. Results have been obtained for the following molecular species adsorbed on several low-Miller-index metal surfaces: CO, $C_2H_2 \rightarrow CCH_3$, C_3H_4, $\rightarrow CCH_2CH_3$ and C_6H_6. The presently available methods should be capable of solving a multitude of molecular adsorbate structures, including large molecules, coadsorbates and disordered species.

1. Introduction

The combination of High-Resolution Electron Energy Loss Spectroscopy (HREELS) and Low-Energy Electron Diffraction (LEED) has been found to be powerful for determining the crystallography of molecular species adsorbed on surfaces. HREELS is particularly convenient for determining the identity of molecular species, by comparison of their vibrational frequencies with those of known molecules, including organometallic clusters [1]. Often, orientational information can also be obtained with HREELS [1]. Knowledge of identity and

orientation markedly simplifies the subsequent LEED analysis, which compares measured with calculated intensities for a large number of still plausible adsorption geometries [2,3]. This allows bond lengths and bond angles to be determined.

The multiple-scattering (i.e. dynamical) nature of LEED complicates structural determinations by strongly increasing the computational cost relative to that of crystallographic techniques based on "kinematic" electron scattering. Therefore, appropriate calculational methods are required to handle the large unit cells and large molecules that can be found at surfaces. In addition, since not all molecules adsorb in an ordered fashion, it is desirable to also perform LEED analyses in the absence of long-range order.

2. Calculational Methods in LEED

LEED theory was designed in the years 1968-1971 for dense, strongly-scattering materials such as metals, in which multiple scattering is dominant [2,3]. Molecular adsorbates are less dense and scatter less strongly, but do not give a kinematic behavior. Therefore, computational savings are to be sought in selective neglect of certain multiple-scattering terms [4].

Since the substrates used today for molecular adsorption are largely the same metals considered in 1968-1971, the full multiple-scattering formalism must be maintained in that part of the surface. Through the "combined-space" [3] method, one may add molecular overlayers treated with suitably approximated formalisms, to be described next.

The simplest case is that of hydrogen atoms, which are such weak scatterers that they can be ignored (unless they are by themselves responsible for a superlattice).

The approximation called "near-neighbor multiple scattering" [4] recognizes that any atom in a molecule is surrounded by few

neighboring atoms, most of which are relatively weak scatterers compared with the situation in the bulk metal. As a result, only a few multiple-scattering paths need to be taken into account. In particular, one may choose to let each segment in such a scattering path link only neighboring, bonding atoms. Accuracy is gradually lost as fewer scattering paths are included. Nevertheless, the ultimate approximation, which treats the molecular layer kinematically, has been used to eliminate many structural models which might appear plausible at first sight [5,6]. Successively more severe approximations do of course reduce the accuracy attainable for the correct structure: the best calculation that can be afforded should be used to refine the best structure which has been identified with more approximate calculations.

One of the computational difficulties with most conventional LEED formalisms is the large number of beams that must be considered when the surface unit cell is large [3]. The computational effort is proportional to the square or the cube of the unit cell area. Molecules are found to frequently order in lattices with untractably large unit cells. Therefore, the "beam-set-neglect" approximation has been designed [7] to avoid this unfavorable scaling law. The resulting computational effort is at worst linear in the unit cell area, and even constant if one so desires.

The beam-set-neglect method can be easily extended to disordered overlayers. The resulting diffuse intensity can be shown to contain the local bonding information (short-range ordering) that one is most interested in with molecular adsorption [8]. Thus, local structure determination is possible with LEED in the absence of long-range order, as it is with SEXAFS, ARPES and other surface-sensitive techniques. This method has been successfully compared to a different theory of diffraction by disordered adsorbates [8,9].

3. Molecular Adsorbate Structures

Only organic molecules have been subjected so far to surface structure

determination by LEED, coupled with HREELS. Carbon monoxide (CO) was found to be a favorable candidate for such work and has served well as a test case for experimental and theoretical procedures. The adsorption sites of CO on metal surfaces were successfully predicted on the basis of the CO-stretch vibration frequencies, using an empirical site assignment derived for metal-carbonyl clusters [10]. Indeed, either the top site or the bridge site occurs in the six CO adsorption structures determined so far: CO on Ni(100) [11], CO on Cu(100) [11a], CO/Pd(100) [12], CO on Rh(111) at two coverages [13,5,6] and CO on Ru(0001) [14].

The other molecular structures determined with LEED concern hydrocarbons having two to six carbon atoms: C_2H_2 (acetylene) on Pt(111) [15], Ni(111) [16] and Ni(100) [17], $\rightarrow CCH_3$ (ethylidyne) on Pt(111) [18] and Rh(111) [19], C_3H_4 (methylacetylene) on Rh(111) [20], $\rightarrow CCH_2CH_3$ (propylidyne) on Rh(111) [21] and C_6H_6 (benzene) on Rh(111) [7]. The complete molecules in this list (C_2H_2, C_3H_4 and C_6H_6) are found to primarily π-bond to the metal surface. For C_2H_2 on Pt(111) and Ni(111), C_3H_4 ($HC{\equiv}C-CH_3$) and C_6H_6 on Rh(111), the unsaturated C-C bonds are parallel to the metal surface. The adsorption site is somewhat uncertain for C_2H_2 on Pt(111) and Ni(111), top and μ-bridge being preferred, respectively. Centering on the hollow site is obtained for C_2H_2 on Ni(100), C_3H_4 on Rh(111) and C_6H_6 on Rh(111). The C_3H_4 molecule is found to be considerably bent, with its methyl ($-CH_3$) group pointing up at an angle of about 35° from the surface plane. This reflects rehybridization due to adsorption and was predicted already for the terminal hydrogens of adsorbed C_2H_2, based on HREELS data [22] and theoretical calculations [23]. Such upward bending of hydrogen is also predicted for adsorbed benzene [24,25].

The alkylidynes (ethylidyne and propylidyne) have been observed on Rh(111) and Pt(111) as products of acetylene or ethylene (C_2H_4) adsorption (for ethylidyne), or of methylacetylene or propylene (C_3H_6) adsorption (for propylidyne). The multiple C-C bond of the parent molecule has become a single bond during hydrogenation or dehydrogenation, oriented prependicularly to the surface. The

adsorbed species are bonded through a carbon atom to three metal atoms surrounding a hollow site. The upper part of the species is a saturated hydrocarbon terminating in a methyl group. In the case of propylidyne, the methyl group is tilted with respect to the surface normal.

4. Prospects

Work is underway in Berkeley on some molecular adsorbate structures whose complexities illustrate the present capabilities of LEED calculations coupled with HREELS. One such structure is naphthalene ($C_{10}H_8$) on Rh(111), which produces both a (3x3) and a ($3\sqrt{3}$x$3\sqrt{3}$) R30° unit cell: these have areas 9 and 27 times that of the (1x1) unit cell and presumably contain 10 and 30 carbon atoms per unit cell, respectively. Another such structure concerns benzene on Pt(111), which can form both a ($2\sqrt{3}$x4)rect and a ($2\sqrt{3}$x5)rect unit cell, with areas 16 and 20 times the (1x1) area, respectively. If, as HREELS indicates, these cells contain 4 and 6 CO molecules, respectively, in addition to the presumed two benzene molecules per cell, one has 20 and 24 atomic scatterers per unit cell, respectively (hydrogen being ignored).

In view of the many structural parameters that these structures contain, it is important to gather complementary information restricting the number of possible structures. Besides HREELS data, one source of information is consideration of Van der Waals radii that identify forbidden molecular overlaps [26]. A more accurate approach to this question comes from force-field calculations, which evaluate more detailed Van der Waals interactions [27]. Also, geometries of adsorbed molecular species may be studied by energy-minimization techniques: for large molecules on extended surfaces, extended Hückel cluster calculations [23,28] or corresponding two-dimensional tight-binding band-structure calculations [25,28] can serve as useful guides.

Another important aspect of the work concerns experimental

procedures. Apart from the standard need for well-defined surface conditions, adsorbed molecules present a special difficulty: great susceptibility to electron-beam-induced damage. New approaches to reduce the LEED beam exposure have been implemented, principally the use of video cameras [29], which shorten the time needed to take the data. A further development, which is about to come into use, replaces the LEED display screen by a position-sensitive detector coupled with micro-channel plates [30]: this allows the intensity of the incident LEED beam to be reduced by a factor of 10^6, essentially eliminating surface damage.

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