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SYMMETRY, SELECTION RULES AND NOMENCLATURE IN SURFACE SPECTROSCOPIES

(IUPAC Recommendations 1996)

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Symmetry, selection rules and nomenclature in surface spectroscopies (IUPAC Recommendations 1996)

Synopsis -- The widespread use of techniques such as vibrational spectroscopy and photoelectron spectroscopy for the investigation of adsorbates on single crystal surfaces has focussed attention on the symmetry properties of adsorbed molecules and on the application of selection rules. In much published work, however, confusion exists as to the appropriate point groups and, in the case of ordered overlayers, the appropriate space groups. In this document, the symmetry properties of clean and adsorbate-covered single crystals are described, appropriate nomenclature suggested and the physical principles leading to selection rules in surface spectroscopies briefly listed.

1. INTRODUCTION

Spectroscopic methods are playing an increasingly important role in surface chemical research. Just as in the case of free molecules, such techniques are based on absorption or scattering experiments involving photons, electrons or other particles. In particular, a low sampling depth is required, giving rise to a high sensitivity to the outermost atomic layers of the solid sample under investigation. For the study of adsorbates on single crystal surfaces with techniques such as vibrational spectroscopy or photoelectron spectroscopy, a knowledge of the symmetry properties of the systems concerned is a necessary prerequisite for applying selection rules (refs. 1-5). In much published work, however, confusion exists as to the appropriate point groups, and in the case of ordered overlayers, the appropriate space groups. Moreover, there is still no single, generally accepted nomenclature for describing ordered overlayers or lettering surface Brillouin zones. Prompted by this situation the present document describes the symmetry properties of clean and adsorbate-covered single crystals, makes recommendations for nomenclature and briefly lists the selection rules in surface spectroscopies as well as the physical principles on which they are based.

The various techniques in surface science that require knowledge of symmetry properties have been described in many books and review articles. References 6 through 8 offer a most recent selection.

2. SYMMETRY PROPERTIES OF SURFACES

2.1 Symmetry Operations at a Solid Surface

Although the abrupt termination of a bulk crystal destroys the three-dimensional periodicity of a solid, the surface region generally retains a two-dimensional periodicity which is important in determining physical properties as well as for diffraction experiments and spectroscopy. It is important to remember, however, that only the symmetry properties are two-dimensional in nature; the surface itself has three-dimensional character incorporating both the immediate sub-surface region (or selvedge) and a possible adsorbate layer. In particular, the surface of a bulk crystal is seldom "ideally terminated": reconstruction and relaxation are likely to occur. The presence of an adsorbate may also induce reconstruction. The following description of symmetry properties applies of course equally well to clean and reconstructed surfaces as well as to surfaces covered with an ordered adsorbate layer. (We exclude from this account effects associated with magnetic ordering.)

Translational symmetry is defined by the vectors ***a*** and ***b*** which have magnitude and direction determined by the unit cell of the two-dimensional crystal lattice. Successive application of the translation operators on any lattice point serves to define a Bravais lattice which is one of the following five types (see Fig. 1):

Oblique	Primitive Rectangular	Centred Rectangular	Square	Hexagonal

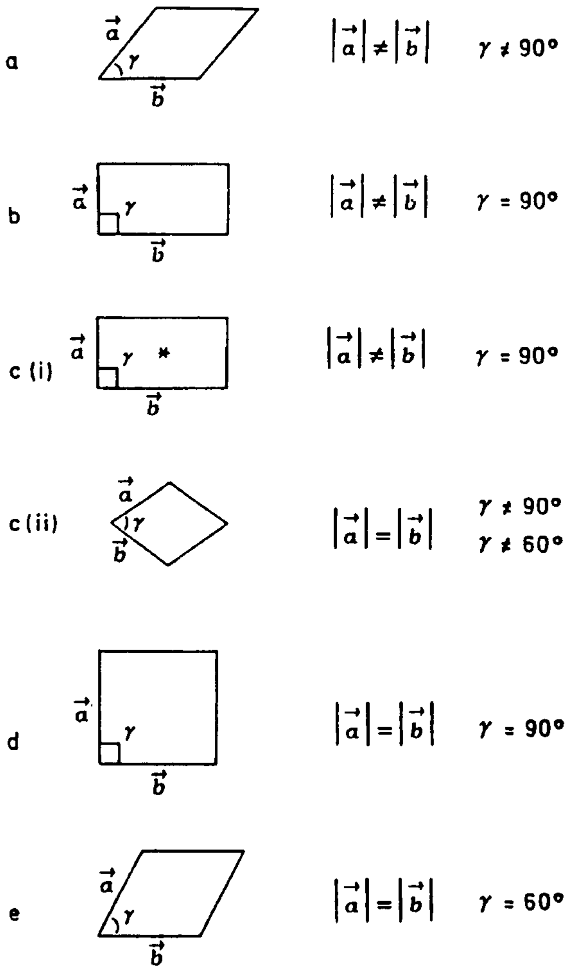

Fig. 1.
The five two-dimensional Bravais lattices.
a) oblique
b) primitive rectangular
c(i) centred rectangular
c(ii) alternative definition of the centred rectangular lattice
d) square
e) hexagonal.

Note that the translation vectors defining the centred rectangular net are not based on a primitive unit cell. An alternative definition of this lattice is given in Fig. 1c(ii) which is based on a primitive unit cell.

Rotation axes (C_n) are required to be perpendicular to the surface and are given (in Schoenflies notation) by (Note a)

$$C_1, C_2, C_3, C_4, C_6.$$

Symmetry planes (Note b) (σ_v) are required to be perpendicular to the surface. **Glide planes** (Note c) ($\sigma_v| \frac{1}{2}t$), involving reflection in a plane combined with translation along the direction of the plane by half a translational period, are also required to be perpendicular to the surface.

Combining the five Bravais nets with these latter symmetry elements leads to 17 plane, or two-dimensional space, groups. The **space group** is thus that collection of symmetry elements, including translation, associated with a particular infinite crystalline structure. In three dimensions there are altogether 230 space groups of which 27 are non-symmorphic, i.e. they contain glide planes and/or screw axes. Of the 17 two-dimensional space groups (Note d) four are non-symmorphic in which glide planes are necessary for the

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Note a: A knowledge of the symmetry elements, symmetry operations, and resulting point groups associated with free molecules is assumed in this document.

Note b: Symmetry planes are often referred to, particularly by physicists, as **mirror** planes.

Note c: In two dimensions, glide planes are frequently referred to as glide lines. The line is the interaction of the glide plane with the surface. The use of the word "line" is, however, strictly speaking incorrect because of the three-dimensional nature of the surface.

Note d: There are further space groups associated with *isolated* two-dimensional arrays but the true two-dimensional space groups (which are applicable to the surface situation) have no symmetry plane or inversion centre in the two-dimensional plane.

TABLE 1. The two-dimensional space groups (after ref. [9]), H-M = Hermann-Mauguin notation; Sch = Schoenflies notation.

No.	Crystal System	Lattice Type	Factor Group H-M	Factor Group Sch	Space Group H-M	Space Group Sch
1	triclinic	oblique	1	C_1	*p*1	C_1
2	monoclinic	oblique	2	C_2	*p*2	C_2
3	monoclinic	rectangular (*p*)	*m*	C_s	*p*1*m*1(*pm*)	C_s^1
4	monoclinic	rectangular (*p*)	*m*	C_s	*p*1*g*1(*pg*)	C_s^2
5	monoclinic	rectangular (*c*)	*m*	C_s	*c*1*m*1(*cm*)	C_s^2
6	orthorhombic	rectangular (*p*)	2*mm*	C_{2v}	*p*2*mm*(*pmm*)	C_{2v}^1
7	orthorhombic	rectangular (*p*)	2*mm*	C_{2v}	*p*2*mg*(*pmg*)	C_{2v}^2
8	orthorhombic	rectangular (*p*)	2*mm*	C_{2v}	*p*2*gg*(*pgg*)	C_{2v}^3
9	orthorhombic	rectangular (*c*)	2*mm*	C_{2v}	*c*2*mm*(*cmm*)	C_{2v}^4
10	tetragonal	square	4	C_4	*p*4	C_4
11	tetragonal	square	4*mm*	C_{4v}	*p*4*mm*(*p*4*m*)	C_{4v}^1
12	tetragonal	square	4*mm*	C_{4v}	*p*4*gm*(*p*4*g*)	C_{4v}^2
13	hexagonal	hexagonal	3	C_3	*p*3	C_3
14	hexagonal	hexagonal	3*m*	C_{3v}	*p*3*m*1	C_{3v}^1
15	hexagonal	hexagonal	3*m*	C_{3v}	*p*31*m*	C_{3v}^2
16	hexagonal	hexagonal	6	C_6	*p*6	C_6
17	hexagonal	hexagonal	6*m*	C_{6v}	*p*6*mm*(*p*6*m*)	C_{6v}

generation of the lattice. Note that some other space groups also contain glide planes but these are necessarily a consequence of other symmetry elements. Screw axes cannot exist in two dimensions. The 17 two-dimensional space groups are listed in Table 1 with both Schoenflies and Hermann-Mauguin ("International") notations and illustrated in Fig. 2. The convention for depicting the space groups, as well as the order of their listing, follow that of the International Tables for Crystallography (ref. 9). The right-hand diagrams give the space groups proper, i.e. the symmetry elements themselves. On the left-hand side is the complete set of equivalent positions that any single point, marked by an open circle, would assume after application of the symmetry operation. A **factor group** is the point group isomorphous with the space group excluding translations. The symmetry elements of the factor group show a one to one correspondence with the symmetry elements of the space group. Glide planes correspond to mirror planes. A **site group** is a point group which consists of the symmetry elements at a particular crystallographic site, the most important ones being where an atom or molecule is centred. The ten possible site and factor groups are listed in Table 2. Note that "point group" is a generic term; factor or site group should be used as appropriate. The irreducible representations of the 17 two-dimensional space groups have been derived by Cracknell (ref. 10).

TABLE 2. The two-dimensional point groups.

Hermann-Mauguin	Schoenflies	Hermann-Mauguin	Schoenflies
1	C_1	4*mm* (4*m*)	C_{4v}
2	C_2	3	C_3
1*m* (*m*)	C_s	6	C_6
2*mm* (*mm*)	C_{2v}	3*m*	C_{3v}
4	C_4	6*mm* (6*m*)	C_{6v}

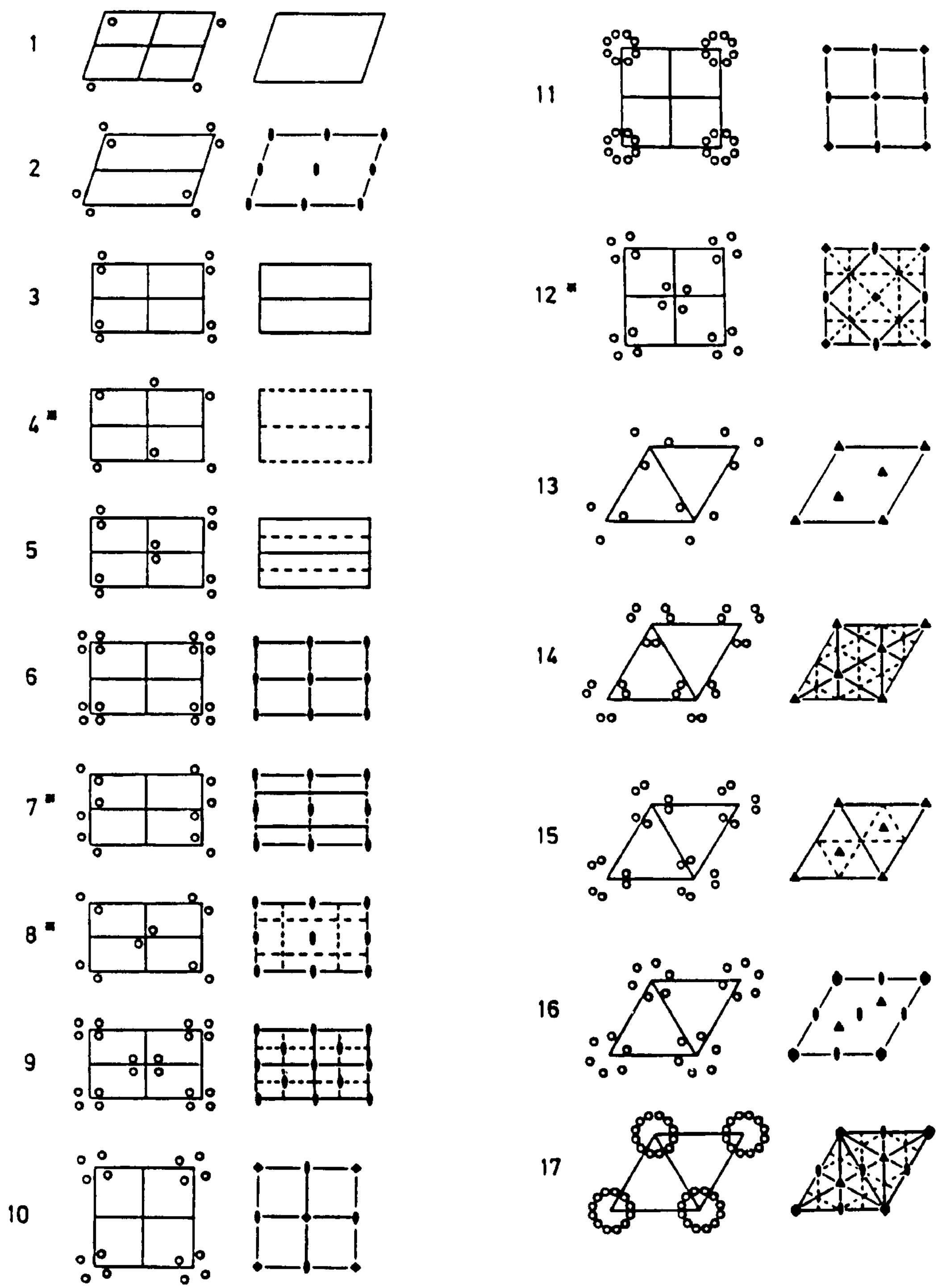

Fig. 2. The 17 two-dimensional space groups. The order of listing of the space groups follows that of Table 1 and thus of the International Tables for Crystallography (ref. 9). An asterisk denotes a non-symmorphic space group. In each case, the figure on the left-hand side shows the equivalent positions which arise from application of the symmetry operations on a given point. The right-hand side figure shows the symmetry elements at all points in the unit cell. Heavy line = symmetry plane; dashed line = glide plane; ellipse = two-fold rotational axis; *n*-sided polygon = *n*-fold rotational axis. A thin line at the boundary of a figure does not denote a symmetry plane.

2.2 Adsorbate Layers - Nomenclature

Due to the nature of the (chemi)sorption bond and the lateral interactions between adsorbed species ("through space" and/or "through substrate"), adsorbate layers are frequently ordered. It is convenient to describe this situation by relating the new, full surface Bravais net ("adsorbate" mesh) to that of the clean, ideally terminated surface prior to adsorption ("substrate" mesh). The most general way is to use the matrix notation (ref. 11). The primitive translation vectors of the adsorbate mesh, $\boldsymbol{a}'$ and $\boldsymbol{b}'$, are related to those of the substrate mesh, $\boldsymbol{a}$ and $\boldsymbol{b}$, by

$$\boldsymbol{a}' = G_{11}\boldsymbol{a} + G_{12}\boldsymbol{b}$$

$$\boldsymbol{b}' = G_{21}\boldsymbol{a} + G_{22}\boldsymbol{b}$$

The four coefficients form a matrix

$$\boldsymbol{G} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

such that the adsorbate and substrate real space nets are related by

$$\begin{pmatrix} \boldsymbol{a}' \\ \boldsymbol{b}' \end{pmatrix} = \boldsymbol{G} \begin{pmatrix} \boldsymbol{a} \\ \boldsymbol{b} \end{pmatrix}$$

For example, benzene and carbon monoxide co-adsorbed on Rh{111} at room temperature form a

$$\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$$

ordered overlayer. The determinant of $\boldsymbol{G}$ is simply the ratio of the areas of the two meshes and can be related to coverage if the number of species in the absorbate mesh is known. Coverage, θ, is usually defined as the ratio of the number density of species in the absorbate layer to that in the outermost layer of the substrate.

In simple cases when the angle between $\boldsymbol{a}'$ and $\boldsymbol{b}'$ is the same as that between $\boldsymbol{a}$ and $\boldsymbol{b}$ the more convenient Wood notation may be used (ref. 12). The relationship is expressed in this case by the ratios of the lengths of the primitive translation vectors, $p = |\boldsymbol{a}'|/|\boldsymbol{a}|$ and $q = |\boldsymbol{b}'|/|\boldsymbol{b}|$, and the angle of rotation θ between the two nets. Thus, for adsorbate A on the $\{h,k,l\}$ surface of the material M (Note e) the recommended notation is

$$\mathrm{M}\{h,k,l\}\ (p \times q)\ \mathrm{R}\theta^{\circ} - \mathrm{A},$$

where Rθ° indicates rotation by θ° to bring the nets into axial registry, e.g., Ni{100}(2 x 2) - O, Pd{111}($\sqrt{3}$ x $\sqrt{3}$)R30° - CO or Cu{100}($\sqrt{2}$ x $\sqrt{2}$)R45° - O. Note that the latter structure is often referred to as Cu{100}c(2 x 2) - O or "centred" (2 x 2). The centred notation should, however, be avoided for a square Bravais net and reserved for the centred rectangular case. Both matrix and Wood notations can be applied to reconstructed surfaces; thus Si{111}(7x7).

For hexagonal substrate lattices, there are adsorbate overlayer structures which, although they cannot be expressed in the Wood notation, can be conveniently and usefully expressed in a so-called "rectangular" notation. These are primitive rectangular structures [p x $q\sqrt{3}$] which in matrix notation are expressed as

$$\begin{pmatrix} p & p \\ -q & q \end{pmatrix}$$

Note e: The $\{h,k,l\}$ surface is a plane surface parallel to the generalized set of $\{h,k,l\}$ planes. Parentheses should be reserved for specific (h,k,l) surfaces; thus {100}, but (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$. Similarly, the $<h,k,l>$ direction refers to a generalized set of directions but brackets are reserved for specific $[h,k,l]$ directions; thus <110>; but [110], [101], [011], $[\bar{1}10]$, etc.

and centred rectangular structures c[p x $q\sqrt{3}$] which are expressed as

$$\begin{pmatrix} \frac{p+q}{2} & \frac{p-q}{2} \\ \frac{p-q}{2} & \frac{p+q}{2} \end{pmatrix}$$

It is recommended in these cases that the structure is defined in the matrix notation as well.

Note that the Wood notation should only be applied to the real lattice, *not* to the reciprocal lattice (see below); its use in reciprocal space can be misleading. Features in low energy electron diffraction patterns should be labelled by their respective indices.

2.3 Stepped and Kinked Surfaces

Two systems of nomenclature are in common use for the description of stepped surfaces. The more straightforward is the standard, Miller indices notation. Alternatively, the surface can be described in terms of a terrace/step notation, $n\{h,k,l\}_t$ x $m\{h,k,l\}_s$. This identifies the terrace and step orientations in terms of the Miller indices of the terrace, $\{h,k,l\}_t$ and step, $\{h,k,l\}_s$ together with the length of the terrace, expressed as the number of rows of terrace atoms, *n*, between step edges, and the height of the step, expressed as the number of atomic planes, *m*, parallel to the terrace plane,which are present at the step. This notation is useful when local, atomic properties, such as the chemisorption site, are discussed. It also distinguishes surfaces with the same macroscopic orientation but differing terrace lengths and, of course, step heights. The nomenclature is, however, only straightforward and unique when low index terrace and steps are involved. It is recommended that the Miller index notation is always given as well.

In the case of kinked surfaces, where the step $\{h,k,l\}_s$ is a higher Miller index face, an improved description of the local surface geometry can then be obtained by further decomposition of the step using the *microfacet* notation (ref. 13). This relates the Miller indices description of the macroscopic orientation to terrace, step and kink orientations in low Miller indices. The description, also applicable to non-kinked, stepped surfaces, has the advantage of treating terrace, step and kink on the same basis and allows the microscopic orientation to be determined unambiguously. Again, however, we recommend that, if the microfacet notation is used, the macroscopic orientation in terms of the high Miller indices should also be quoted.

2.4 The Reciprocal Lattice

The two-dimensional reciprocal lattice is not only important for interpreting diffraction data but also for understanding the electronic and vibrational properties of surfaces and adsorbed layers. In the case of an ordered overlayer the overlap of adsorbate wavefunctions will produce two-dimensional Bloch states and make a band description of the electronic structure more appropriate. The same is true of vibrational wavefunctions which will form surface phonon bands. These states - both vibrational and electronic - will be characterized by their parallel momentum, or parallel component of wave-vector, $\boldsymbol{k}_{\parallel}$, in the two-dimensional reciprocal lattice. The primitive translation vectors of the reciprocal lattice, $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$, are related to those of the real lattice $\boldsymbol{a}$ and $\boldsymbol{b}$ by

$$\boldsymbol{a}\cdot\boldsymbol{a}^* = 1, \qquad \boldsymbol{b}\cdot\boldsymbol{b}^* = 1$$

and

$$\boldsymbol{a}^*\cdot\boldsymbol{b} = 0, \qquad \boldsymbol{b}^*\cdot\boldsymbol{a} = 0.$$

The reciprocal lattice will thus have the same type of Bravais net as in real space. The relationship between the real and reciprocal lattice is shown in Fig. 3 for the oblique case. Although this picture is instructive the oblique net has little symmetry; Fig. 4 thus shows the reciprocal net for a rectangular array. Since points in reciprocal space are related by

$$\boldsymbol{k}'_{\parallel} = \boldsymbol{k}_{\parallel} \pm \boldsymbol{g}_{hk}$$

where $\boldsymbol{g}_{hk}$ is a reciprocal lattice vector, the Bloch states or phonons can be located according to their position in the Surface Brillouin Zone (SBZ) in a so-called extended zone scheme also shown in Fig. 4. In spectroscopy it is often important to know the point group at various points of the SBZ as well as the

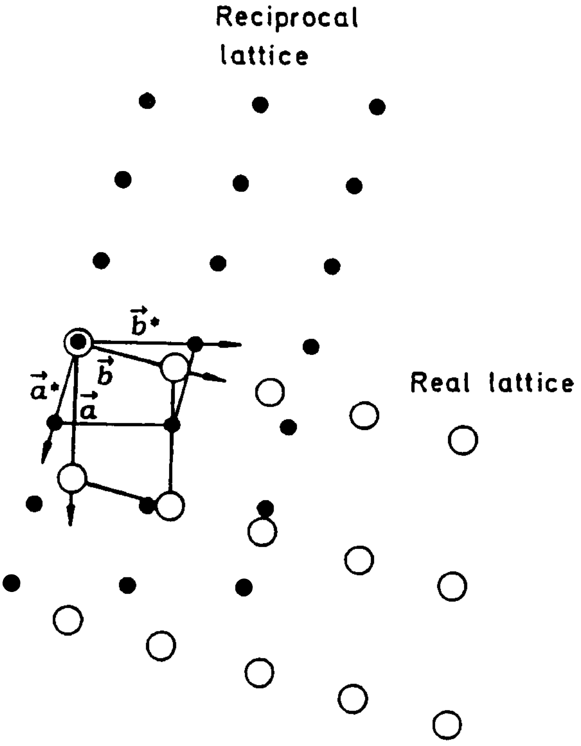

Fig. 3. Schematic diagram of the relationship between the real and reciprocal lattice for the oblique net.

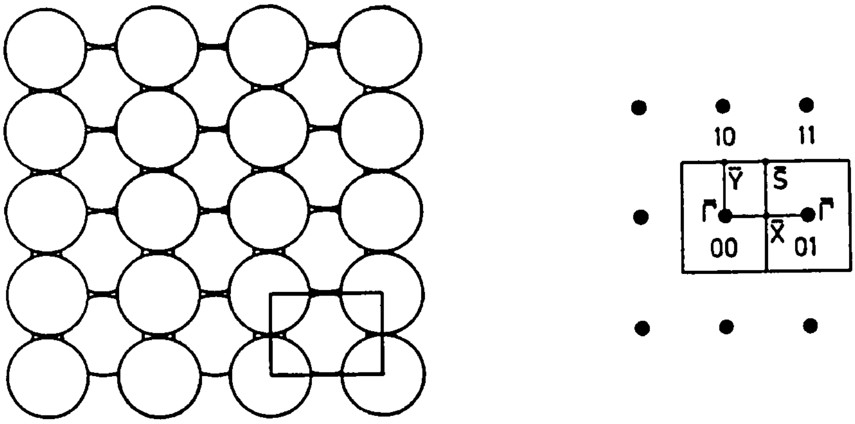

Fig. 4. The fcc{110} surface in real space (left) and in reciprocal space (right). The surface Brillouin zone is also shown.

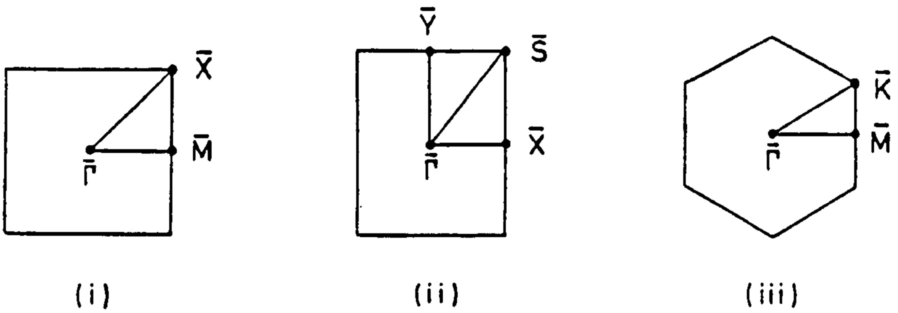

Fig. 5. Surface Brillouin zones for the (i) square, (ii) rectangular and (iii) hexagonal Bravais lattices. The nomenclature for the centred rectangular and oblique lattices follow from the rectangular and hexagonal cases.

representations to which the Bloch states or phonons belong. At the centre, $\bar{\Gamma}$, the factor group will be appropriate. The symmetry points and directions should all carry a "bar" to distinguish them from the corresponding symbols in the three-dimensional Brillouin zone of the bulk crystal. The recommended nomenclature for the square, rectangular and hexagonal Bravais lattices is shown in Fig. 5.

2.5 Molecules Adsorbed at Surfaces

Imperfect substrate surfaces, low adsorbate coverage or disordered adsorbate layers can lead to the situation where there is no identifiable space group symmetry. In such situations, the use of factor groups and/or site groups is strictly inappropriate. Nevertheless, the symmetry properties of the molecule and its immediate substrate environment may still dominate spectroscopic behaviour. The possible point groups remain those given above for the factor and site groups.

In certain spectroscopies, even the influence of the immediate environment may be sufficiently weak that an effective point group of higher order may be appropriate. For example, in the adsorption of a diatomic molecule such as CO on the {110} face of an fcc metal surface with its molecular axis perpendicular to the surface, the maximum possible symmetry would seem to be given by the point group C_{2v} even in the high symmetry sites. This would imply a splitting of the 1π occupied molecular orbital into b_1 and b_2 components. In fact, photoelectron spectroscopy has never been able to detect such a splitting of the 1π level. In other words, the behaviour is equally well described by employing the point group $C_{\infty v}$ and ignoring the real lateral structure of the surface. A higher symmetry point group may thus be appropriate because at an intrinsic level the splitting is too small compared to the band width arising from the lifetimes of the states involved or because, at an extrinsic level, the experimental resolution of a particular spectrometer or spectroscopic technique is insufficient.

3. SELECTION RULES FOR ELECTRONIC EXCITATIONS AT SURFACES

3.1 Photoabsorption, Electron Energy Loss Spectroscopy

Optical transitions in the valence region can be observed in VUV (vacuum ultraviolet) reflection spectroscopy or in electron energy loss spectroscopy. Assuming that dipole scattering also dominates in electron loss (i.e., when the primary beam energy is much greater than the energy loss and scattering is in the specular direction), the matrix element governing the transition contains the term $|\langle\psi_f|\mu|\psi_i\rangle|$, where ψ_i and ψ_f are the initial and final state electronic wavefunctions. Dipole selection rules for transitions in adsorbed molecules may therefore be derived in the normal way using the product theorem. Whereas in the case of vibrational excitation both the ***E*** vector (and necessarily the dipole appearing on the molecule) are almost *completely* screened parallel to the surface, this effect is not so pronounced for electronic excitations. A transition with a dipole aligned parallel to the surface is expected to be reduced by a factor of $|\hat{\varepsilon}(\omega)|^2$, where $\hat{\varepsilon}$ is the complex dielectric function at frequency ω relative to one of the same magnitude oriented perpendicular to the surface. In the VUV the reduction factor could be as high as 10 but reduces to ≈ 1 in the soft X-ray region. At low electron energies, and particularly for off-specular scattering, dipole- and spin-forbidden transitions may also occur in electron loss spectroscopy because of non-zero momentum transfer.

In the case of core level excitations observed in soft X-ray photoabsorption of molecules on surfaces (NEXAFS = near edge X-ray absorption fine structure or XANES = X-ray absorption near edge structure), dipole selection rules (Note f) have proved very useful in structural studies. Early investigations showed that the transitions (e.g. $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ in molecules containing C, N and O atoms) are strongly polarized. The presence of a rotation axis and/or the azimuthal orientation of a symmetry plane can be established by changing the direction of the ***E*** vector. Surface screening, as mentioned above, is negligible.

Note f: The concept of **symmetry breaking** may be applied in core level photoabsorption. For a benzene molecule adsorbed parallel to the surface, for example, the site group can be at most C_{6v}. In such a case the creation of the deep hole is then considered as lowering the symmetry to C_s, upon which basis the selection rules can be determined.

3.2 Photoelectron Spectroscopy (Photoemission)

In this experiment - the most powerful method of probing valence level states of adsorbates - the same type of dipole matrix element, $|\langle\psi_f|\mu|\psi_i\rangle|$, applies as in photoabsorption. Whereas in photoabsorption (or when appropriate in the photoionization cross-section) the experiment integrates essentially over all possible final states, in angle-resolved photoemission the final state $|\psi_f\rangle$ is uniquely specified by its energy and momentum, or wavevector, $\boldsymbol{k}_f$. For certain geometries selection rules can thus be derived. In the case of normal emission, for example, observation of photoemission features is necessarily restricted to those transitions for which $|\psi_f\rangle$ belongs to the totally symmetric representation, i.e., the partial waves comprising the final state wavefunction may only be s, p_z, d_{z^2} etc. in character. Similar arguments can be applied for emission in symmetry planes where the final state must be symmetric with respect to reflection. The initial state ψ_i can be a molecular wave function or a two-dimensional Bloch state located at a non-general point in the surface Brillouin zone. We then consider the Cartesian components of the matrix element $\langle\psi_f|\mu_x|\psi_i\rangle$, $\langle\psi_f|\mu_y|\psi_i\rangle$ and $\langle\psi_f|\mu_z|\psi_i\rangle$. Different weighting can be given to these by appropriate choice of the polarization and/or angle of incidence of the photon beam. For example, in the case of CO adsorbed on a Ni{100} surface, when plane polarized light is incident along the surface normal and emission is observed in a plane perpendicular to the plane of polarization, then emission from the $\widetilde{4\sigma}$ and $\widetilde{5\sigma}$ orbitals is not observed and only the $\widetilde{1\pi}$ orbital emission is seen in the spectrum. (The tilde indicates that the adsorbate molecular orbital has been modified by the interaction with the substrate.)

When a surface molecule has a rotation axis and multiple scattering in the final state can be neglected, a further possibility emerges. For totally symmetric initial states the emission plane can be treated as a symmetry plane and the selection rules applied. This is known as the "one hole, central potential approximation" or as the "atomic dipole approximation".

All the statements above apply accordingly to inverse photoemission, or Bremsstrahlung isochromat spectroscopy.

3.3 Penning Ionization Spectroscopy

There appear to be no simple selection rules associated with Penning ionization spectroscopy at surfaces.

4. SELECTION RULES FOR VIBRATIONAL EXCITATIONS AT SURFACES

4.1 Infrared Reflection-Absorption Spectroscopy

The matrix element governing the transition contains the term $\langle\psi_f|\mu|\psi_i\rangle$ where ψ_i and ψ_f are now the initial and final state vibrational wavefunctions. At metal surfaces, observable modes are those which cause a dipole moment change in the component perpendicular to the surface; the parallel components are screened by the metal electrons. Active modes, therefore, are those belonging to the totally symmetric representation of the relevant site or factor group. Since excitation involves no significant momentum exchange with the surface, the observed excitations are at the centre ($\bar{\Gamma}$) of the two-dimensional Brillouin zone.

As an example, CO adsorbed on a Cu{100} surface occupies an on-top site in a ($\sqrt{2}$ x $\sqrt{2}$)R45° structure. The relevant site group is C_{4v} and the C-O stretch and Cu-C stretch are the totally symmetric (A_1) vibrations.

4.2 Electron Energy Loss Spectroscopy

Dipole scattering: The scattered electron may interact with the long range dipole field of the surface, in which case the selection rules are the same as those governing infrared reflection-absorption spectroscopy, providing there is metallic screening. Only those modes producing a change in the perpendicular component of the dipole moment are active. Dipole excitation results in electrons being scattered very near to the specular direction. Furthermore, scattering in this direction is dominated by the dipolar interaction, when the dynamic dipole moment is large.

Impact scattering: The cross-section for impact scattering depends upon a term $\langle\boldsymbol{q}\cdot\boldsymbol{u}\rangle$ where $\boldsymbol{q}$ is the momentum change of the electron during scattering and $\boldsymbol{u}$ is the vibrational amplitude. This results in the following selection rules:

i) If the system has a two-fold rotational axis, modes anti-symmetric with respect to this axis can only be observed off-specular.

ii) If the scattering plane containing the incident beam, the reflected beam and the surface normal is a symmetry plane of the system, then vibrational modes anti-symmetric with respect to reflection in this plane are inactive.

iii) If the scattering plane, defined in (ii), is perpendicular to a symmetry plane of the crystal, then modes polarized perpendicular to this plane can only be observed off-specular.

4.3 Raman Spectroscopy

The following description refers to normal, non-enhanced Raman spectroscopy. The active modes are those which give rise to a change in the α_{zz} component of the polarizability, where z is the surface normal. This dominance of the α_{zz} component arises, as in the case of infrared selection rules, from the screening properties of metal surfaces. However, because the screening is less efficient at ultraviolet and visible frequencies than it is at infrared frequencies, modes transforming as α_{xz} and α_{yz} may be observable but at reduced intensity relative to the α_{zz} modes. The fully active modes, which cause a change in the α_{zz} polarizability component, necessarily belong to the totally symmetric representation of the relevant point group. For surface-enhanced Raman spectroscopy see, e.g., Ref. 14.

4.4 Inelastic Atom and Inelastic Scattering Neutron Spectroscopies

These techniques for measuring the vibrational properties of surfaces are related to impact scattering in electron energy loss spectroscopy (EELS). The scattering cross-section depends on the term $<\boldsymbol{q}\cdot\boldsymbol{u}>$ linking the vibrational displacement, $\boldsymbol{u}$, with the momentum change of the scattered particle, $\boldsymbol{q}$. The selection rules are the same as for impact scattering in EELS and, in particular, for scattering in a mirror plane of the system, only those modes polarized in that plane are spectroscopically active.

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