



## VIBRATIONAL SPECTRUM OF VICINAL SURFACES

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### Abstract

The vibrational spectrum of FCC metal vicinal surfaces is obtained from displacement-displacement Green's functions. Results are presented for the Pt(332) surface. Surface spectral densities are calculated, in the neighbourhood of the surface, for selected directions in the Brillouin zone. The coherent surface vibrations contain features that reproduce the available experimental results and predict others that might be observable by He scattering. The dispersion relation of a high frequency surface mode is calculated. The surface mode frequency is shown to depend weakly on the wave-vector along high symmetry lines in the surface Brillouin zone. The polarization and local character of this mode are closely related. Near the Brillouin zone centre and also near the zone boundary it is strongly polarized perpendicularly to the surface and a sudden polarization change is seen when its frequency approaches the surface projection of the bulk spectrum.

Surface vibrations keep a close relationship to the local chemical environment and to the geometrical arrangement of surface atoms. For this reason the study of surface spectra may provide a great deal of information on relaxation and reconstruction processes and it has become a valuable tool to characterize metallic and semiconductor surfaces. It is also possible to explore surface vibrations to obtain basic information on adsorption on clean surfaces.

In the last decade a comprehensive analysis of vibrational properties of low Miller indexes (LMI) metal surfaces was carried out.<sup>1-5</sup> The cornerstone of this achievement is no doubt the recent sophistication in the experimental techniques with high surface sensitivity. The inelastic scattering of He atoms and the off-specular electron-energy-loss spectroscopy are among the most important experimental techniques to analyze surface vibrations.<sup>2-3</sup> With these techniques a complete sampling of the surface modes throughout the Brillouin zone is now possible, and this has encouraged a great deal of investigation on LMI metal surfaces. The basic picture that emerges from the recent literature regarding LMI surfaces is that local modes and resonances, as observed experimentally, can be reproduced satisfactorily by central force constant models. Furthermore, relaxation processes have been reported and generally involve the first two surface planes.<sup>1-2</sup>

Vicinal surfaces are obtained by cleavage at small angles relative to a LMI direction. These surfaces, as a result, have high Miller indexes (HMI) and their geometrical structures differ in many respects from those of LMI surfaces. They are very open structures, therefore atoms of deep planes participate in many surface processes. The stacking of planes with large unit cells

densely packed determine their unique catalytic properties.<sup>6-7</sup>

The geometrical arrangement of atoms near a vicinal surface resemble wide terraces oriented along LMI directions limited by steps which are typically a few lattice constants in height. There is a weak coupling between atoms in the same plane as compared to the interaction involving atoms in different planes. As a result any analysis must take into account a number of inequivalent atoms (or planes) and a rich structure of modes near the surface is expected.

Vicinal surfaces play a central role in the understanding of heterogeneous catalysis.<sup>6</sup> Despite the great technological interest they have had relatively little theoretical attention. One of the major difficulties is the possible charge rearrangement involving a relatively big number of planes in the surface region. As opposed to LMI surfaces, in vicinal surfaces relaxation processes may include more than just a couple of planes.

We report a study of the vibrational properties of vicinal surfaces. The emphasis is on building a scheme which is valid for any crystallographical orientation based on the knowledge of the interplane couplings. The method provides a clear theoretical framework in which key features of the surface vibrations may be analyzed. It incorporates in a very simple manner the effect of the coordination of the atoms near the surface as well as possible force constant changes.

In order to establish a general scheme for vicinal surfaces, we begin by studying a clean kinkless stepped surface. Reconstruction and relaxation effects, as well as adsorbed atoms, may be considered by simply modifying the equations of motion for the Green's functions in the surface region.

We assume no reconstruction, therefore the translational symmetry parallel to the surface allows a transformation to a basis of plane waves  $\{n, k\}$  propagating in each plane ( $n=0$  is the surface plane and  $n > 1$  for deeper planes). Spectral densities, properly weighted by the polarization vector component in each plane, may be obtained from selected displacement-displacement Green's functions<sup>8</sup>. The Green's function equations of motion are given by

$$(Mw^2 - \Phi_{00}(k))G_{00}(k) = 1 + \sum_j \Phi_{0j}(k) G_{j0}(k)$$

$$(Mw^2 - \Phi_{jj}(k)) G_{j0}(k) = \sum_m \Phi_{jm}(k) G_{m0}(k) \quad (j>0) \quad (1)$$

In eq.(1) above the summations are done over the set of planes coupled together. It is an infinite set of matrix equations in which each entity is a 3x3 matrix.  $\Phi_{jm}$  describe the coupling between waves  $(jk)$  and  $(mk)$ , both propagating in the direction specified by the wave number  $k$  (parallel to the surface) and localized in planes  $j$  and  $m$ . It is convenient to adopt the concept of principal layer<sup>9</sup> in order to condense the notation.

A principal layer consists of the minimum number of adjacent planes defined in such a way as to have only coupling between adjacent layers. In the following we incorporate the plane index within a principal layer in the matrices representing the Green's functions and interlayer/intralayer couplings. If  $N$  is the number of planes in a principal layer the relevant matrices have order  $3N$ .

The size of a principal layer depends on two different factors. One has a purely geometrical origin and is related to the interplane spacing. The second factor is the range of the interaction between atoms in the lattice. The equations of motion for the surface layer Green's function then read

$$(Mw^2 - H_{00}(k)) g_{00}(k) = 1 + H_{01} g_{10}(k)$$

$$(Mw^2 - H_{nn}(k)) g_{n0}(k) = H_{nn-1}(k) g_{n-10}(k) + H_{nn+1}(k) g_{n+10}(k) \quad (n \geq 1) \quad (2)$$

where, for instance, the matrix elements of  $H_{00}(k)$  are obtained from the interplane/intraplane matrices  $\Phi_{jp}(k)$  for  $j, p = 0, 1, 2, \dots, N-1$ . If no relaxation is considered all the matrices but  $H_{00}(k)$  are constant.  $H_{00}(k)$  incorporates the incomplete coordination near the surface.  $g_{00}(k)$  includes all the Green's functions in the first layer, namely:  $G_{1m}(k)$  for  $1, m=0, 1, 2, 3, \dots, N-1$ . From  $g_{00}(k)$  we may obtain the spectral densities in the first  $N$  planes. The spectral densities in the surface plane, for instance, are obtained from the first three diagonal elements:

$$\rho_{ii}(w, k) = -(2Mw/\pi) \text{Im}(g_{00}(k))_{ii} \quad (i=1, 2, 3) \quad (3)$$

Transfer matrices, defined by  $g_{n+10}(k) = T(k) g_{n0}(k)$ , are used to decouple the infinite set of equations (2),  $T(k)$  satisfies

$$(Mw^2 - H_{11}(k)) T(k) = H_{10}(k) + H_{12}(k) T(k)^2 \quad (4)$$

To obtain  $T(k)$  we use the renormalization technique of Goncalves da Silva and Koiller<sup>10</sup> and Sancho and coworkers.<sup>11</sup> This is a rapidly convergent method which is specially important for vicinal surfaces because we are then dealing with sparse but very large matrices. It is a general feature of vicinal surfaces that an atom in a given plane is coupled to atoms in a few other planes, not necessarily being coupled to atoms in the intermediate ones. Therefore the matrices  $H_{nm}(k)$  may have 3x3 blocks of zeros.

The calculation proceeds by using  $T(k)$  in eq.(2) to obtain the surface layer Green's function. From this Green's function we obtain spectral densities in all planes of the surface layer. At this point we turn to a particular vicinal surface.

In the last decade a few theoretical works have been dedicated to study local modes of the Pt(332) surface.<sup>12-14</sup> These works followed the publication by Ibach and Bruchmann<sup>15</sup> of EELS spectra reporting a high frequency mode ( $205 \text{ cm}^{-1}$ ) above the bulk Pt spectrum ( $195 \text{ cm}^{-1}$ ). The experiment samples the coherent surface vibrations, which dominate the induced dipole moment, and is conclusive in assigning the local nature of the mode.

The theoretical reports so far, present local and spectral surface densities for selected propagation vectors. The calculation for the  $\Gamma$  point<sup>12</sup> reproduce the frequency of the local mode reported in reference 15. It is nevertheless worth pursuing a systematic search for arbitrary wave vectors. The reason underlying this is that only a single surface mode frequency value is available from experiment. The comparison of the theoretical predictions with the experimental results on this basis is already satisfactory, but we may add theoretical information in order to explore the fine details of the surface structure.

Vicinal surfaces may exhibit a variety of surface excitations (local modes), as well as surface resonances, and it is necessary to have theoretical results that go beyond the existing information from experiment. In this way other details of the surface vibrational properties may be studied and the theoretical predictions may be placed alongside with new experimental data in order to quantify the changes near the surface. In this respect there is a particular interest in characterizing surface relaxation from the force constant changes near the surface.

We performed calculation of surface spectral densities throughout the Brillouin zone and analyzed empirically possible models of relaxation involving variation of force constants in the surface region.

The geometry of the surface is displayed in fig.1. It consists of (111) terraces, of width  $5a/\sqrt{2}$ , containing six inequivalent atoms, limited by  $(1\bar{1}\bar{1})$  steps of height  $5a/\sqrt{88}$ , where  $a$  is the lattice constant. The coordinate axis are oriented as follows:  $x-(\bar{1}10)$ ,  $y-(\bar{1}\bar{1}3)$  and  $z-(332)$ . The  $x$ -axis is oriented along the step edge and the normal to the surface is  $z$ . We adopted a central force model restricted to first neighbour atoms. The principal layer contains six planes and the matrices in eqs.2-5 are of order 18. The step edge and corner atoms (1 and 6 in fig.1) occupy special positions and are expected to play a key role in relaxation processes. Atom 1, in the first plane, has the lowest coordination and atom 6, the last in the surface principal layer, is more strongly coupled to

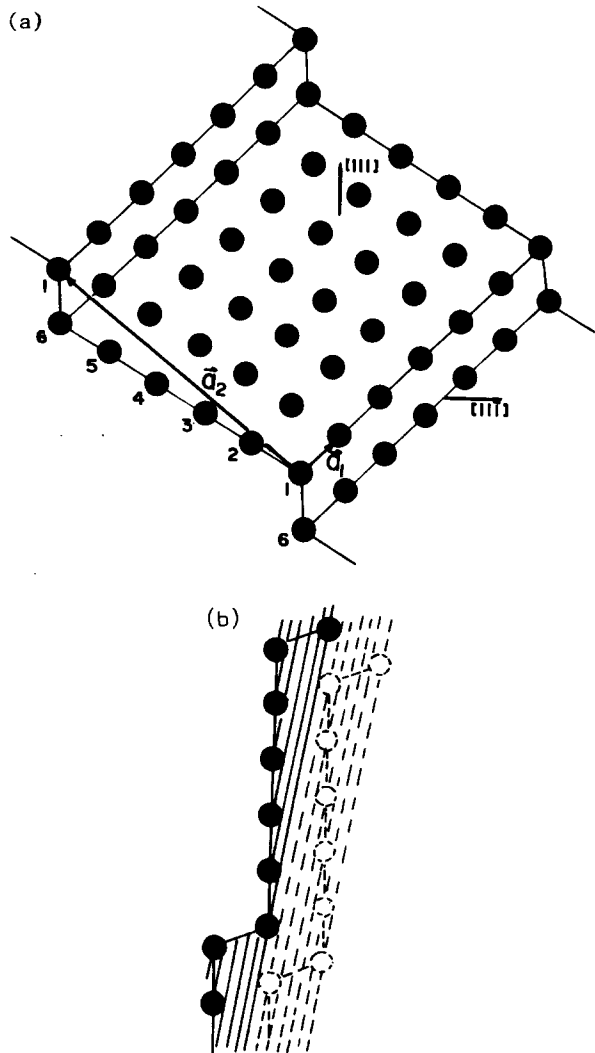


Figure 1  
Geometrical structure of the Pt(332) surface. In (a) we show the (111)

terraces and (11 $\bar{1}$ ) steps, indicating the inequivalent atoms: atom 1 at the step edge, atoms 2,3,4 and 5 in the (111) terrace and atom 6 in the step corner. In

(b) we show the stacking of (332) planes as viewed in the (110) direction, indicating in full lines the surface layer and in dashed lines the first layer below.

the layer underneath than to the surface layer itself. The terrace atoms (2,3,4,5 in fig.1), on the other hand, are in an environment that resembles the (111) surface.

Ibach and Bruchmann's results suggest strengthening of the force constants near the surface. We examined various possibilities for relaxation within the surface layer. To reproduce the experimental results all the interactions involving the step edge atom and the corner atom were increased by 40%. This kind of relaxation produce modifications in force constant matrices within the first two layers, namely:  $H_{00}(\mathbf{k})$ ,

$H_{10}(\mathbf{k})$ ,  $H_{01}(\mathbf{k})$  and  $H_{11}(\mathbf{k})$ . Therefore the transfer matrix apply from layer  $n=1$  and the eqs.(2) lead to

$$g_{00}(\mathbf{k}) = (Mw^2 - H_{00}(\mathbf{k}) - H_{01}(\mathbf{k}) \\ (Mw^2 - H_{11}(\mathbf{k}) - H_{12}(\mathbf{k})T(\mathbf{k}))^{-1} H_{10}(\mathbf{k}))^{-1} \quad (5)$$

Figures 2,3 and 4 contain our main results. For comparison purposes the bulk spectrum for a given

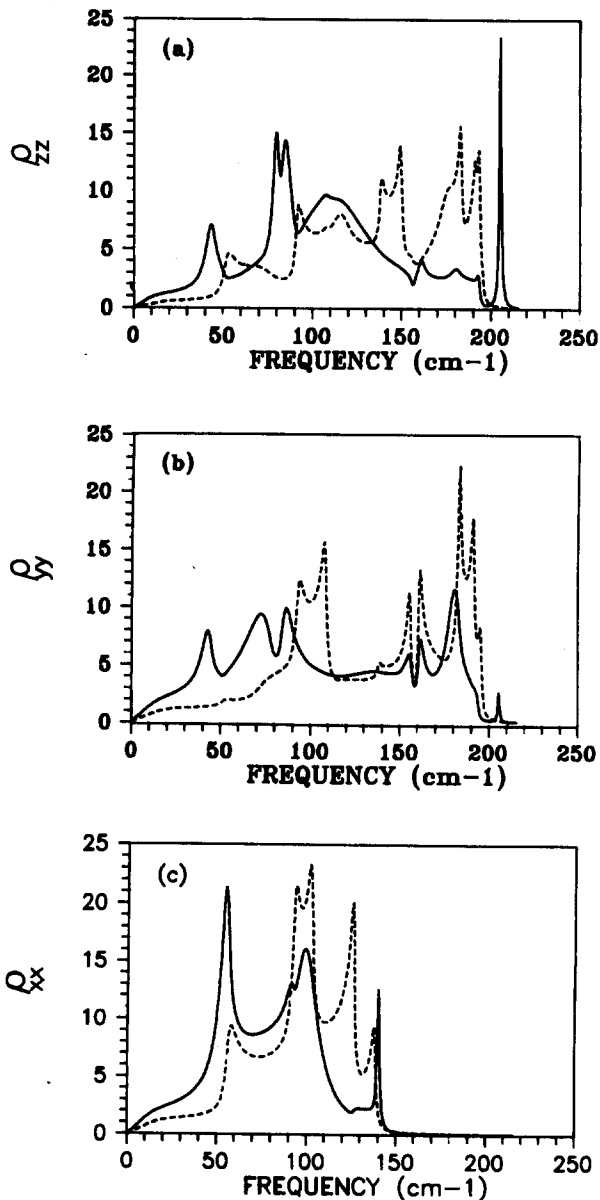


Figure 2  
We show the surface plane spectral densities for  $\mathbf{k}=0$ , the bulk spectral densities are also shown (in dashed lines) for comparison. (a) Atomic motions normal to the surface ( $z$ -direction), (b) atomic motions along the (11 $\bar{3}$ ) direction and (c) atomic motions along the step edge ( $x$ -direction).

$k$ -vector was also calculated, with the help of another transfer matrix  $Q$ , which deals with the propagation to the surface. The expression for  $Q$  is similar to that quoted by Sancho et al<sup>11</sup> for  $T$  with  $t$ 's and  $t$ 's interchanged, so that at the same time two transfer matrices are obtained.

The coherent surface vibrations are shown in figs.2 and 3. The leading features of the surface spectrum are the 205  $\text{cm}^{-1}$  local mode and a strong resonance at 140  $\text{cm}^{-1}$ . The high frequency mode (205  $\text{cm}^{-1}$ ) corresponds both in polarization and frequency value to the experiment reported in reference 15. It is worth

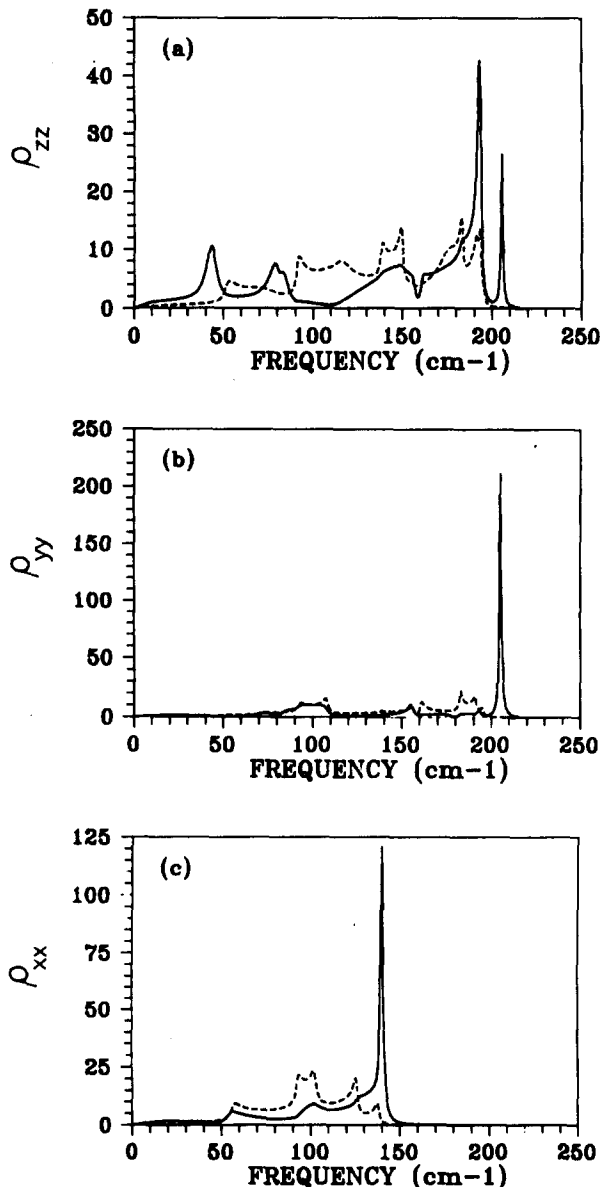


Figure 3  
Spectral densities for atomic motions in the sixth plane from the surface (step corner atom) projected in the coordinate axis described in the caption of fig.2

noticing the polarization change of the local mode from the step edge atom (mainly  $z$ ) to the corner atom (practically  $y$ ). It is also seen that the resonance is extremely localized in the step corner atom and is built up from a singularity in the top of the bulk spectrum ( $x$ -polarization). A direct comparison with experiment is not possible for this mode because the experimental results concentrate on the high frequency range limit.

From figs.2-3 we can also observe that there is a nonnegligible projection of the bulk spectrum into the surface. However strong modifications (transfer of weight, absence of bulk singularities etc) are present. It is interesting to see that these modes may elude the observation of surface features. For instance the  $y$ -polarized vibrations are dominated, in the surface plane, by the projection of bulk modes. On the other hand the vibrations of the step corner atom are totally dominated by surface modes.

Spectral densities were calculated along the  $\Gamma X$  (the step edge direction) and  $\Gamma Y$  lines of the surface Brillouin zone. The dispersion relation of the local mode was obtained by tracing the poles of the surface layer Green's function in planes 0 and 5. Along the  $\Gamma Y$  line the dispersion is very small and the mode is above the bulk spectrum all the way from the  $\Gamma$  point to the  $Y$  point.

As shown in fig.4 the dispersion relation along the  $\Gamma X$  line is also very flat. Despite the small dispersion this result is of great interest. It shows that local surface densities are not adequate to model an angle resolved experiment, such as EELS. From the dispersion relation, extending from 195  $\text{cm}^{-1}$  to 205  $\text{cm}^{-1}$ , we expect a surface band with strong peaks at 205  $\text{cm}^{-1}$ , 195  $\text{cm}^{-1}$  and 201  $\text{cm}^{-1}$  (the local mode frequency at the  $X$  point). This band is located right on the top of the bulk spectrum. It is not, therefore, appropriate to draw any conclusion regarding the experimental results reported in reference 15.

The polarization of the local mode is mainly perpendicular to the surface, with a smaller  $y$  projection, throughout most of the  $\Gamma X$  line. This is so in the region where the local mode frequency is above the bulk spectrum. However a sudden change of polarization is observed when the frequency approaches 195  $\text{cm}^{-1}$ . In this region the mode is polarized in the  $x$  direction. The bulk modes in the same region are strongly  $x$ -polarized

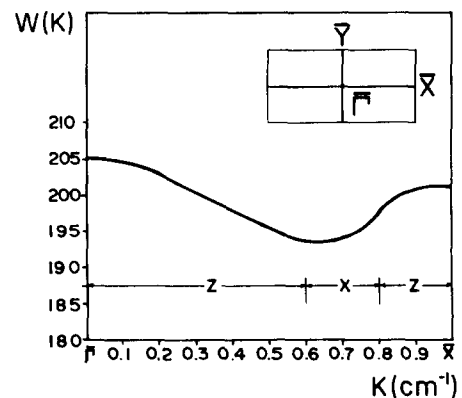


Figure 4  
Dispersion relation of a local surface mode along the  $\Gamma X$  line. The surface Brillouin zone is shown in the inset, and the major polarization component of the surface mode is indicated.

with a small  $y$ -component. Therefore the polarization change conforms with the resonance nature of the mode in this frequency range. This feature can be checked by He atom scattering. It is well known<sup>4</sup> that the scattering cross section for He atoms is dependent upon the phonon polarization and that the vibrations perpendicular to the surface are more effective in the scattering. Therefore by choosing the sagittal plane containing the  $\Gamma X$  line one may be able to use the intensity of scattered He atoms to infer the polarization of the local mode.

We have presented a theory for the phonon spectrum of vicinal surfaces based on the knowledge of interplane couplings. The spectral densities are obtained

from Green's functions which are calculated using a very efficient numerical algorithm. Therefore any HMI surface may be studied without any substantial difficulty. Furthermore the description of the dynamics of the surface atoms may be extended to other models, and reconstruction and relaxation processes may be included. It is worth mentioning that surface mode frequencies and polarizations are very sensitive to relaxation effects and to the lack of coordination of surface atoms. Furthermore the direction of propagation may be crucial to determine the surface mode frequencies. These features are included in the present analysis that we hope will contribute to motivate experimental investigation on vicinal surfaces.

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