

**NOVEL FEATURES OF POTASSIUM AND SODIUM VIBRATIONS ON
COPPER SURFACES OBSERVED BY HIGH-RESOLUTION ELECTRON-
ENERGY-LOSS SPECTROSCOPY**Costanza Astaldi, Petra Rudolf and Silvio Modesti*
Laboratorio TASC-INFM, Padriciano 99, I-34012 Trieste, Italy*(Received May 25, 1990 by Erio Tosatti)*

High-resolution electron-energy-loss spectra of alkali metals adsorbed on Cu show three unexpected features: the adsorbate-substrate stretching frequency does not change with coverage, within 1 meV on Cu(111) and Cu(110), in agreement with the covalent picture of chemisorption; the spectra show an unusual overtone which is interpreted as a consequence of a strongly non linear relationship between the surface dipole moment and the adsorbate-substrate distance; the dynamical dipole moment is strongly coverage dependent.

The properties of alkali metal overlayers on metallic surfaces have generally been explained on the basis of the charge transfer model¹⁻⁴. According to this picture the bond between an alkali atom and the metal substrate is mainly ionic at low coverages, i.e. long nearest neighbor distances between adsorbed atoms, and becomes covalent at high coverages. This change in bonding results from the partial filling of the alkali atom s resonance which, with increasing coverage, is shifted across the Fermi level by the larger depolarization field of the neighboring adsorbed atoms.

In contrast with this model, self consistent calculations⁵⁻⁷ have shown that the bond between the substrate and the alkali atom is covalent at all coverages and that the charge transfer is negligible.

Recent photoemission and inverse photoemission studies of alkali metal overlayers on Al(111)^{8,9} reported an energy shift of the s and p resonances as the coverage is increased. This was interpreted either as the transition from ionic to covalent bonding^{8,9}, corroborating the charge transfer model, or, in agreement with the self consistent calculations, as the first direct observation of the increase of adatom bandwidths¹⁰. Moreover, photoemission studies of W and Ag core levels^{11,12} have not found any evidence for charge transfer from the adsorbed alkali atoms to the substrate at any coverage, supporting the covalent picture.

A different test for the validity of the calculation on which this picture is based is provided by the vibrational spectroscopy of the alkali overlayer: Ishida, in fact, predicts for Na on jellium⁶ only a slight decrease of the stretching frequency (17 meV) as a function of Θ . Even if no surface phonon calculation has been done in the framework of the charge transfer model, it is plausible to expect a sensible change in the vibrational spectrum as the surface bonding changes from ionic to covalent. An example of the changes in the vibrational properties of surface systems induced by variations of the ionicity of the surface bond is provided by the SEXAFS and HREELS studies of S and Cl on Ni(100) and Cu(100)¹³.

In the present work we report on a high-resolution electron-energy-loss spectroscopy (HREELS) study of the vibrational spectra of Na and K on Cu(100), Cu(111) and unreconstructed Cu(110) (Na and K dosed at 90 K) measured at Γ . We find no coverage dependence of the Na-Cu stretching frequency on all surfaces (within our experimental accuracy, i. e. 1 meV). The K-Cu vibrational frequency is constant on Cu(111) and Cu(110) and depends only slightly on Θ on Cu(100) for $\Theta < 0.02$. The scattering cross section per alkali atom is instead found to decrease by more than one order of magnitude when the alkali-alkali distance decreases. This behavior is much more dramatic than what is expected from the built-up of the depolarization field due to long range electrostatic interaction between adsorbates¹⁴, pointing to the occurrence of a large charge redistribution at about 1/5 of the saturation coverage. Furthermore we observe an additional peak in the HREELS spectra at an energy twice that of the alkali metal - Cu stretching mode. The intensity of this peak and the absence of higher order overtones indicate that this loss cannot be due to an anharmonicity of the potential energy curve. We interpret it therefore as a result of the strong non linearity of the alkali dipole moment as a function of adsorbate-substrate distance.

The Cu (100), (111) and (110) surfaces were oriented within 0.7° and cleaned through cycles of Ar⁺ sputtering at 550 K and annealing at 700 K until no contaminants were detected by Auger spectroscopy and sharp LEED spots were observed.

The HREELS spectrometer, a standard ELS 22, was operated at a working pressure of 4×10^{-11} mbar with an energy resolution of 4-6 meV. The spectra were taken with primary energies of 2.2 and 1.7 eV in the specular direction (incidence angle 60°). The samples were biased to compensate for work function changes. Cleaning, alkali metal deposition and sample characterization were carried out in a separate chamber. The alkali metals were evaporated from SAES dispenser sources at a rate of 10^{-3} - 10^{-2} ML s⁻¹ (ML = monolayer). The pressure during evaporation was never higher than 3×10^{-10} mbar and dropped to 1×10^{-10} mbar after turning off the source.

The HREEL spectra were measured within 30 minutes from the alkali metal deposition and showed no trace of

* also at Dipartimento di Fisica, Università degli Studi di Trieste, Via A. Valerio 2, I-34127 Trieste, Italy

contaminants (CO, H, O). After longer exposure to residual gasses we observed changes in the intensities of the peaks (especially at high alkali coverages), but not in their energies. These changes were related to the appearance of contaminant peaks in the loss spectra.

EELS spectra of the K 3p core level to conduction band excitations were taken using a 4 grid LEED apparatus with an energy resolution of about 0.5 eV and primary energy of 100 eV.

The coverage Θ , defined with respect to the density of copper atoms in the topmost atomic layer, was determined by measuring the ratio R of the intensity of K (Na) Auger signal at 250 eV (990 eV) and the 920 eV Cu Auger signal. The proportionality constant between R and Θ was calculated by using the assumption that the first change of slope in the R vs. evaporation time curve occurs at the completion of the first layer, which corresponds to $\Theta \approx 0.6$ ($\Theta \approx 0.8$) for K (Na) on Cu(110) and $\Theta \approx 0.3$ ($\Theta \approx 0.5$) for K (Na) on Cu(111)¹⁵. On the Cu(100) surface the hexagonal and $c(2 \times 2)$ LEED patterns observed for the K (corresponding to $\Theta \approx 0.316$) and Na saturation coverage respectively, were used to determine the proportionality constant.

Fig. 1 shows some typical HREELS spectra of the clean and alkali metal covered Cu surfaces measured at 300 K (Cu(100) and Cu(111)) and 90 K (Cu(110)). The spectrum of the clean Cu(110) substrate (curve a) is characterized by a surface phonon resonance at 20 meV¹⁷. After dosing Na (K) (Fig. 1 curves b, d, f and c, e, g for Na and K respectively) a much stronger and broader peak at about 18 meV (12 meV) appears, reaches its maximum intensity at about 1/6 of the saturation coverage and then decreases without shifting in energy (see Fig. 2, 3 and 4). At the same time the average nearest neighbor distance between adsorbates decreases roughly as $\Theta^{-1/2}$ on Cu(111) and as Θ^{-1} in the direction of the troughs of Cu(110)¹⁸. Since the ratio of the vibrational frequencies corresponding to the Na- and the K- induced peaks is very close to the inverse of the

square root of the ratio of the alkali metal masses, and the loss intensities are strongly peaked in the specular direction, the observed peaks can be straightforwardly attributed to the dipole active adsorbate-substrate stretching mode.

The results for the vibration energies and the anelastic scattering cross sections of the alkali metals induced losses are summarized in figures 3 and 4 respectively. These values have been obtained fitting the elastic peak and the loss with gaussians. Clearly evident is the independence of the adsorbate-substrate frequency on the coverage (within our experimental accuracy, i.e. 1 meV), with the only exception of K on Cu(100), where a 3 meV upward shift is observed for $\Theta < 0.02$. These results are in agreement with Ishida's calculations⁶ and they therefore support his picture of covalent bonding between the alkali atoms and the substrate. We estimate that the maximum amount of upward shift in frequency with coverage due to dipole-dipole interaction is less than 1 meV for both adsorbates¹⁹.

On all the surfaces the intensity of the stretching induced peak, normalized to the intensity of the elastic peak, increases roughly linearly with coverage only for coverages less than 1/5 of the saturation coverage. A drastic drop in intensity occurs at higher coverages and at 1/3 of the saturation coverage the scattering cross section per alkali atom is more than ten times smaller than at 1/10.

This behavior can not be explained considering only long range dipole coupling between the alkali atoms with a constant dynamical dipole moment: in fact, the dashed line in Fig. 4 a) represents the intensity computed in this framework¹⁹ and diverges strongly from the experimental data. Since the scattering cross section is proportional to the square of the alkali atom dynamical dipole moment²⁰, the strong coverage dependence of the loss intensities points to a large redistribution of the charge in the alkali atoms as the coverage is increased. The electron density rearrangement is also testified by the sharp decrease of the static dipole moment per alkali atom at coverages higher than 1/10 of the saturation coverage (for Cu(110) see ref.21) and by the abrupt drop (about 0.3 eV) of the K3p binding energy we

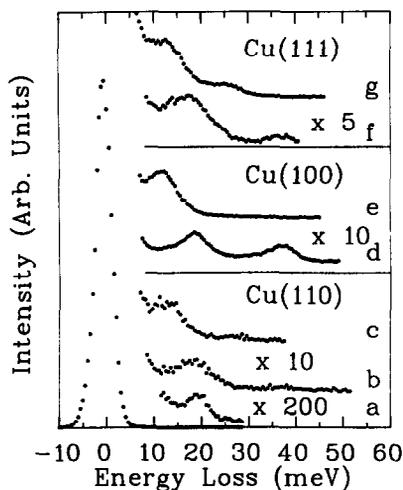


FIG. 1 HREELS spectra of alkali metal covered Cu surfaces. The spectra are normalized to the elastic peak intensity. Cu(110): (a) clean surface; (b) $\Theta_{Na} = 0.13$; (c) $\Theta_K = 0.08$; Cu(100): (d) $\Theta_{Na} = 0.18$; (e) $\Theta_K = 0.01$; Cu(111): (f) $\Theta_{Na} = 0.12$; (g) $\Theta_K = 0.05$.

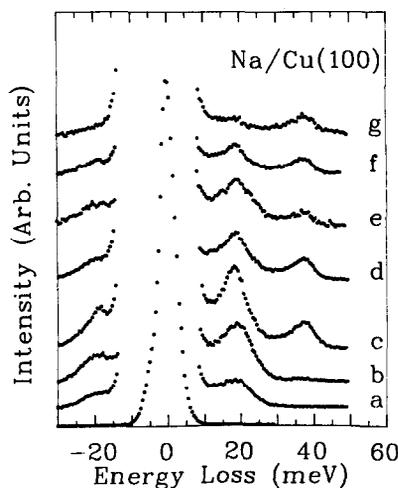


FIG. 2 HREELS spectra of Na/Cu(100) normalized to the elastic peak intensity. The scaling factor for each spectrum is indicated in brackets. (a) $\Theta_{Na} = 0.01$ (x 20); (b) $\Theta_{Na} = 0.04$ (x 20); (c) $\Theta_{Na} = 0.07$ (x 20); (d) $\Theta_{Na} = 0.12$ (x 20); (e) $\Theta_{Na} = 0.14$ (x 20); Cu(111): (f) $\Theta_{Na} = 0.17$ (x 20); (g) $\Theta_{Na} = 0.4$ (x 40).

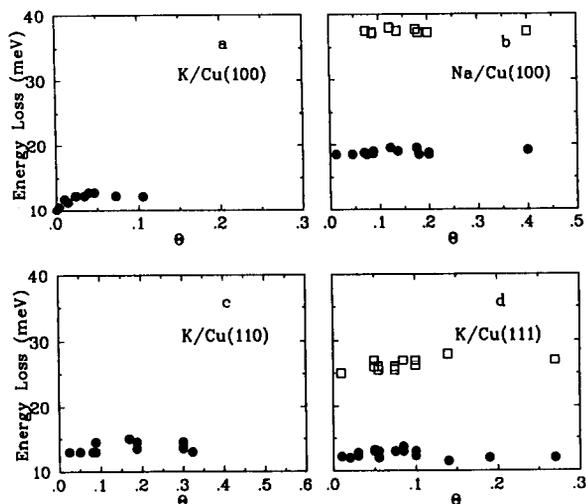


FIG. 3 Energy of the alkali metal stretching peaks (dots) and of their overtones (squares) as a function of coverage for: (a) K/Cu(100), (b) Na/Cu(100), (c) K/Cu(110) and (d) K/Cu(111).

have found at same coverage on the Cu(110) surface. According to Ishida's calculations, the charge redistribution is related to the formation of alkali-alkali bonds and does not affect the nature of the adatom-substrate bond⁶⁻⁷.

An additional strong peak at an energy twice that of the stretching peak is observed at coverages higher than 1/6 of the saturation coverage for Na and K on Cu(111) and Na on Cu(100) (see squares in Fig. 3 and 4). Detailed studies of the loss spectra in an extended energy range gave no evidence for higher order overtones²². The overtone cannot be explained as a result of a double scattering process, since its relative intensity is clearly not proportional to the square of that of the first loss.

The possibility that the overtone is due to the presence of a strong anharmonicity in the potential energy as a function of adsorbate-substrate distance d can be excluded on the basis of the following arguments: For increasing coverage, our data show that the curve of the potential energy as a function of d maintains a constant curvature at its minimum, while the depth of this minimum decreases, as testified by the reduction of the desorption energy²³ when the alkali atom overlayer becomes denser. Therefore the anharmonicity must increase with coverage. This is in agreement with the observed change in the relative intensities of the two peaks. However this explanation is ruled out by the intensity ratio between the second and the first peak (up to 1): assuming a Morse potential for the alkali metal energy as a function of d , such a ratio corresponds to an anharmonicity parameter, χ_e , close to 1²⁴; this value is two orders of magnitude larger than that obtained from the desorption energy of similar systems (1 - 2 eV)²³.

The correct explanation for the origin of the second peak has therefore to be sought in the strong nonlinearity of the

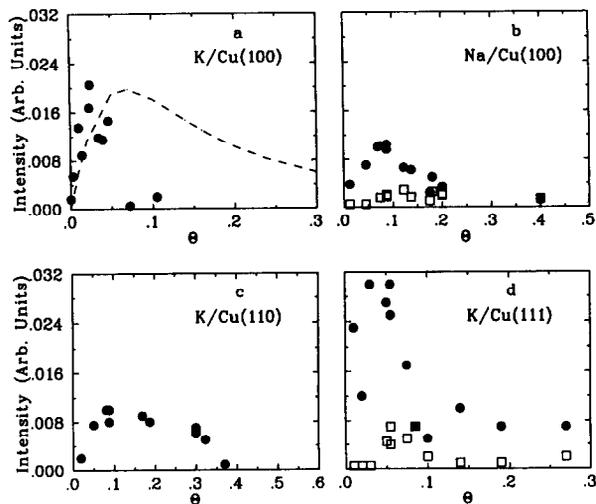


FIG. 4 Intensity of the alkali metal stretching peaks (dots) and of their overtones (squares) as a function of coverage for: (a) K/Cu(100), (b) Na/Cu(100), (c) K/Cu(110) and (d) K/Cu(111). Dashed line in (a): see text. The data are normalized to the elastic peak intensity.

electric dipole moment with d : the dipole moment of an alkali atom is large (about 10 Debye⁴) at its equilibrium distance from the surface, but vanishes when the alkali atom is far away from the substrate or when the adsorbate is incorporated into the metal. As a consequence, the response function of the alkali overlayer should contain terms at overtone frequencies even if the potential were perfectly harmonic. At intermediate and high coverages on the close packed surfaces the intensity of the overtone is comparable to that of the single phonon peak (see Fig. 4 b and d). This implies that the quadratic term in the dipole moment versus d relationship should be comparable to the linear term for displacements around the equilibrium position of the order of 0.1 Å (zero point displacement).

Since we could not find any evidence for a third overtone, the cubic term in the dipole moment versus d relationship must be negligible.

In conclusion we have found that the alkali metal stretching frequency does not change with coverage on the Cu(111) and Cu(110) surfaces, in agreement with the covalent picture of chemisorption. A second loss is observed at an energy twice that of the alkali metal - substrate stretching mode for coverages higher than 1/6 of the saturation coverage. We suggest that this overtone peak is related to a strongly nonlinear term in the relationship between the dynamical dipole moment and the alkali metal position.

Acknowledgement - The authors would like to thank Prof. F. Tommasini and Prof. E. Tosatti for many helpful discussions and Gilio Sandrin for technical assistance. The partial financial support of this project by AREA di Ricerca is gratefully acknowledged.

REFERENCES

1. R. W. Gurney, *Phys. Rev.* **47**, 479 (1935)
2. N. D. Lang, *Phys. Rev.* **B4**, 423 (1971); N. D. Lang and A. R. Williams, *Phys. Rev.* **B18**, 616 (1978)
3. J. P. Muscat and D. M. News, *Solid State Comm.* **11**, 737 (1972); *J. Phys.* **C7**, 2630 (1974); J. P. Muscat and I. P. Batra, *Phys. Rev.* **B34**, 2889 (1986)
4. T. Aruga and Y. Murata, *Progress in Surf. Sci.* **31**, 61 (1989)
5. E. Wimmer, A. J. Freeman, J. R. Hiskes and A. M. Karo, *Phys. Rev.* **B28**, 3074 (1983)
6. H. Ishida, *Phys. Rev.* **B38**, 8006 (1988); H. Ishida and K. Terakura, *Phys. Rev.* **B38**, 5752 (1988)
7. H. Ishida, *Phys. Rev.* **B39**, 5492 (1989)

8. K.-H. Frank, H.-J. Sagner and D. Heskett, *Phys. Rev. B* **40**, 2767 (1989)
9. K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins and A. M. Bradshaw, *Phys. Rev. Lett.* **61**, 2488 (1988)
10. H. Ishida, *Phys. Rev. Lett.* **63**, 1535 (1989); reply by K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins and A. M. Bradshaw, *Phys. Rev. Lett.* **63**, 1536 (1989)
11. M. Riffe, G. Wertheim and P. Citrin, *Phys. Rev. Lett.* **64**, 571 (1990)
12. S. Modesti, C. T. Chen, Y. Ma, G. Meigs, P. Rudolf and F. Sette, to be published
13. F. Sette, T. Hashizume, F. Comin, A. A. MacDowell and P. H. Citrin, *Phys. Rev. Lett.* **61**, 1384 (1988) and references therein; in these systems a 0.2\AA increase of the ionicity parameter Δr_1 is related to a 20% decrease of the vibrational frequencies and to an even larger variation of the mean square amplitude of the thermal vibrations of the adsorbates.
14. H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, 1982, page 98 ff.
15. We checked this procedure by measuring the lattice parameter of the incommensurate hexagonal alkali metal overlayers on Cu(111) by LEED: see R. L. Gerlach and T. N. Rhodin, *Surf. Sci.* **17**, 32 (1969); W. C. Fan and A. Ignatiev, *J. Vac. Sci. Technol.* **A7**, 2115 (1989)
16. T. Aruga, H. Tochiyama and Y. Murata, *Surf. Sci.* **158**, 490 (1985)
17. J. A. Stroscio, M. Persson, S. R. Bare and W. Ho, *Phys. Rev. Lett.* **54**, 1428 (1985)
18. Cu(111): W. C. Fan and A. Ignatiev *Phys. Rev. B* **37**, 5274 (1988); Cu(110): W. C. Fan and A. Ignatiev *Phys. Rev. B* **38**, 366 (1988)
19. See H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, 1982, page 98 ff.; the polarizability was taken from Ref. 4, Fig. 2.5
20. M. Persson, *Physica Scripta* **29**, 181 (1984)
21. B. Woratschek, W. Sesselmann, J. K ppers, G. Ertl and H. Haberland, *Phys. Rev. Lett.* **55**, 1231 (1985)
22. The first overtone has also been observed, with a much lower intensity, on all the other surfaces.
23. H. P. Bonzel, *Surf. Sci. Reports* **8**, 43 (1987) in references therein
24. H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, 1982, page 268 ff.