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Vibrations of alkali metal overlayers on metal surfaces

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Abstract

We review the current progress in the understanding of vibrations of alkalis adsorbed on metal surfaces. The analysis of alkali vibrations was made on the basis of available theoretical and experimental results. We also include in this discussion our recent calculations of vibrations in K/Pt(111) and Li(Na)/Cu(001) systems. The dependence of alkali adlayer localized modes on atomic mass, adsorption position and coverage as well as the dependence of vertical vibration frequency on the substrate orientation is discussed. The square root of atomic mass dependence of the vertical vibration energy has been confirmed by using computational data for alkalis on the Al(111) and Cu(001) substrates. We have confirmed that in a wide range of submonolayer coverages the stretch mode energy remains nearly constant while the energy of in-plane polarized modes increases with the increase of alkali coverage. It was shown that the spectrum of both stretch and in-plane vibrations can be very sensitive to the adsorption position of alkali atoms and substrate orientation.

1. Introduction

Adsorption of alkali metal atoms on metal surfaces causes a drastic change in many of the properties of metal substrate surfaces. In particular, this adsorption frequently results in the formation of complex crystal structures, which involve certain restructuring of the substrate surface atoms [1–3]. It leads to the modification of the substrate surface electronic states [4, 5] and gives rise to the adsorbate (adlayer) induced electron states [4–12]. It was found that adsorbed alkalis produce charge transfer to the substrate [13–15] and change surface dipoles and electric fields [16]. It was also shown that adsorption of alkalis on metal surfaces enhances the reactivity of these surfaces, making these systems interesting for heterogeneous catalysis [17, 18].

If the substrate has a local band gap in the direction perpendicular to the surface, electrons are reflected from the substrate and can be trapped in quantum well states (QWSs),

which are mostly localized in the adlayer area. Formation of these quasi-two-dimensional electronic states confined to a narrow surface region has, in particular, been observed for Na and Cs adsorption on Cu(111) [7, 9–11, 19]. Long-lived excited states have been reported for small, moderate and full monolayer coverages of alkali atoms on Cu(111) [11, 20–23]. The adsorption of alkalis on metal substrates influences electron–electron [24, 25] and electron–phonon [25, 26] scattering in excited electron and hole states leading often to a change of the decay mechanisms of an excited electron or/and hole [23]. A microscopic understanding of these and related phenomena is important because of their impact on processes such as vibrational excitations, surface scattering, photochemical reactions and charge and energy transport on surfaces.

Similar to creation of electron QWSs the alkali adsorption gives rise to new vibrational states related to the alkali overlayer (adatoms) [27–31]. The adsorption also modifies

surface vibrational states of the metal substrate [28, 32]. In the last decade extensive studies of vibrational properties have been performed for alkalis on metal surfaces. Many of these studies have been done for low coverages of alkalis when interaction between adatoms can be safely ignored (for a review see [34] and references therein). It was shown both experimentally and theoretically that even at very low coverages a stretch (z -polarized) vibrational mode arises [27, 29]. With increasing number of alkali atoms, for moderate and full monolayer coverages, this mode does not normally change its energy [32]; however, it gradually decreases its intensity [27]. Different behavior has been found for the frustrated translation (T) mode [32, 35]. This mode, polarized in the plane parallel to the surface, changes its energy with the coverage increase. Both these modes, being sensitive to the alkali atom adsorption sites, can be used for analysis of the adsorption geometry for different coverages and the dependence of these modes on the adsorption sites. Some discussion of the dependence of a stretch mode energy on the atomic mass of the alkali species has been given by Jacobi *et al* [33] and Finberg *et al* [34]. However, the role of the adsorption site and subsurface orientation in this dependence has not been specified. In this work we present new calculation results for Pt(111)-($\sqrt{3} \times \sqrt{3}$)-K and Pt(111)-p(2 \times 2)-K as well as for Li and Na on Cu(001)-c(2 \times 2) and discuss in detail the dependence of both stretch and T modes on atomic mass, adsorption position and coverage of alkali atoms. We also discuss the dependence of frequency on the substrate orientation. In these discussions we use experimental and theoretical data taken from publications listed in table 1.

The paper is organized as follows. In section 2 we discuss the frequency dependence of both z - and in-plane-polarized modes on alkali species by using the Al(111) and Cu(001) substrates as examples. In section 3 the dependence of the z -polarized and frustrated translation modes on the alkali coverage is analyzed. The frequency dependence on the adsorption position and the substrate orientation is the subject of sections 4 and 5, respectively. Conclusions are given in section 6.

2. Dependence of vibrations on alkali atom mass

In this section we give a comparative survey of the effect of different alkali species on adatom vibrations. As was mentioned above, Finberg *et al* [34] have shown from the analysis of the experimental data that the energies of the vertical vibration mode are scaled approximately as the inverse square root of the alkali adatom mass. However, this qualitative statement was made on the basis of experimental results for different surfaces and coverages. In order to analyze the role of the mass factor itself, it is desirable to consider vibrations of different alkali adatoms in the same conditions (adsorption sites, coverage, and surface orientation). Systems of 1/3 ML of Li, Na, and K on the Al(111) surface are a good example to discuss the alkali mass dependence factor: in all these systems the substitutional adsorption at room temperature has been found and a number of experimental and theoretical studies of vibrations in these systems has been performed (see table 1).

The substitutional adsorption for 1/3 ML of lithium on the Al(111) surface was first suggested by Nagao *et al* [36] from HREELS measurements of the vibrational spectra of this system. Then, using low-energy electron diffraction measurements [37], it was shown that Li adsorption leads to the formation of a binary surface alloy, Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Li. This structure was found to be qualitatively the same as the corresponding Na phase [38–41]. Similar results have also been obtained for 1/3 ML of potassium on the Al(111) surface [42–45]. The only difference is that lithium leads to smaller surface corrugation than the larger alkali atoms do because of the smaller radius. The experimental results have been supported by *ab initio* total energy calculations based on density functional theory [38, 42, 43].

Nagao *et al* [31] have carried out a detailed experimental investigation of the surface phonon dispersion for Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na along the $\bar{\Gamma}K'$ symmetry direction. They found two acoustic modes: $R1$, with a frequency of 12.5 ± 0.2 meV at the $\bar{\Gamma}$ point, and a strongly dispersing mode $R2$ above the bulk phonon edge. Another surface localized mode has been observed at the BZ boundary below the bulk continuum (see figure 2). The phonon mode at the $\bar{\Gamma}$ point was assigned to a resonance characterized by a vertical motion of adatoms (Na and Li).

Vibrational modes of alkalis on Al(111) have also been studied by using the HAS technique [34] for various Na and K adsorption structures including the ($\sqrt{3} \times \sqrt{3}$)R30° one. Finberg *et al* [34] have found vertically polarized modes along the $\bar{\Gamma}K'$ direction and near the BZ edge at 9.2 meV and 6.4 meV for Na and K, respectively.

Ishida and Morikawa [46] considered the Na adsorption on a jellium with the electron density of Al to study the structural and vibrational properties over a wide coverage range. The stretching frequency of the Na-jellium bond which corresponds to the vibration of all the adatoms in phase relative to the substrate has been obtained from the curvature of the total energy as a function of the bond length at equilibrium. In contrast to the experimental results, this frequency was found to decrease monotonically with increasing coverage. This discrepancy results from the simplified structure of the surface. Another theoretical study, the *ab initio* pseudopotential calculation, was performed by Neugebauer and Scheffler [29], who considered the vibration of adatoms against a rigid substrate. They have evaluated the adsorption energy as a function of adsorbate height above the unrelaxed Al(111) surface and then estimated the stretching frequency of the adatom vibration normal to the surface as 12.4 meV.

Investigation of the vibrational and structural properties of the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-AM (AM = Li, Na, K) adsorbed systems with alkalis in substitutional sites was performed in [28] using interatomic interaction potentials from the embedded-atom method. It was found that in Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-AM superstructures a few modes appear below the bulk spectrum (see figure 2). They mostly correspond to vibrations of the topmost substrate layer and adlayer atoms, except for the case of Li, where they are localized on the substrate. Comparing these results with

Table 1. Adsorption structures and phonons in alkali metal adsorbed systems. (HREELS—high-resolution electron energy loss spectroscopy. HAS—helium atom scattering. TRSHG—time resolved second-harmonic generation. LEED—low-energy electron diffraction. EAM—embedded atom method. DFT—density functional theory. FC—force constant model.)

Systems	Coverages and structures	Adsorption sites	Phonons	
			Expt	Calc.
Li/Al(001)	$c(2 \times 2)$	Subst.		EAM [66]
Na/Al(001)	$c(2 \times 2)$	Hollow <i>LT</i> Subst. <i>RT</i>		EAM [66] EAM [66]
Li/Al(111)	$\Theta = 0.03\text{--}1.0$ $(\sqrt{3} \times \sqrt{3})$	Subst.	HREELS [36]	EAM [28]
Na/Al(111)	$(\sqrt{3} \times \sqrt{3})$	Subst.	HREELS [31, 36], HAS [34]	EAM [28], DFT [29], FC [31]
K/Al(111)	$(\sqrt{3} \times \sqrt{3})$	Subst.	HAS [34]	EAM [28], DFT [29]
Cs/Al(111)	$(\sqrt{3} \times \sqrt{3})$ $(2\sqrt{3} \times 2\sqrt{3})$	Top <i>LT</i> Subst. <i>RT</i>	HAS [34] HAS [34]	
Li/Cu(001)	$\Theta = 0.04\text{--}0.8$ $c(2 \times 2)$	On-surf. Hollow	HREELS [59]	EAM ^a
Na/Cu(001)	$\Theta = 0.1$ $\Theta = 0.0\text{--}0.4$ $\Theta = 0.0\text{--}0.5$ $\Theta = 0.05$ $c(2 \times 2)$	Hollow	HAS [78] HREELS [58] HAS [79, 35] HAS [80]	EAM ^a
K/Cu(001)	$\Theta = 0.07$ $\Theta = 0.02\text{--}0.11$	Hollow	HAS [80] HREELS [58]	
Cs/Cu(001)	$\Theta = 0.08$ $\Theta = 0.27$ (1 ML)	On-surf. Quasi-hex.	HAS [80] HAS [56]	
Li/Cu(110)	$\Theta = 0.04\text{--}0.8$	On-surf., reconstr.	HREELS [59]	
Na/Cu(110)	$\Theta = 0.13$	On-surf., reconstr.	HREELS [74]	
K/Cu(110)	$\Theta = 0.02\text{--}0.32$	On-surf., reconstr.	HREELS [74]	
Li/Cu(111)	$\Theta = 0.025\text{--}0.5$	On-surf.	HREELS [75]	
Na/Cu(111)	$\Theta = 0.075\text{--}0.3$ $p(3 \times 3)$, $p(2 \times 2)$, $(\sqrt{3} \times \sqrt{3})$, $(3/2 \times 3/2)$ 1 ML	Hollow Hollow	HREELS [60, 75]	EAM [32] Jellium model [46], DFT [61]
K/Cu(111)	$\Theta = 0.02\text{--}0.27$ $\Theta = 0.08\text{--}0.4$	On-top On-top	HREELS [58] HREELS [60, 75]	
Cs/Cu(111)	2–5 ML		HAS [76]	
K/Ni(001)	2–5 ML		HAS [76]	
K/Ni(110)	$\Theta = 0.2$	On-surf.	HREELS [81]	
Na/Pt(111)	$\Theta = 0.05$	On-surf.	HAS [82]	
K/Pt(111)	$\Theta = 0.02\text{--}0.15$ (2×2) $(\sqrt{3} \times \sqrt{3})$	Hollow	HREELS [62, 63] TRSHG [64] TRSHG [64]	EAM ^a EAM ^a , DFT [65]
Cs/Pt(111)	$\Theta = 0.22\text{--}0.41$	On-surf.	TRSHG [83]	
Na/Mo(001)	$\Theta = 0.0\text{--}0.45$	On-surf.	HREELS [84]	
Cs/Ru(0001)	$c(2 \times 2)$ $\Theta = 0.03\text{--}0.24$ $\Theta = 0.08\text{--}0.25$	On-top <i>RT</i>	LEED [85, 86] HREELS [87] HREELS [33]	

^a Present work.

those measured along the $\overline{\Gamma K'}$ symmetry direction for the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na structure [31] one can suppose that the surface state *S1* found in the experiment has a mixed Al-Na character. The adlayer localized modes, most of which are accompanied by the motion of substrate atoms, are located in the bulk continuum for Li adsorption and lie only beneath the bulk phonon spectrum (except for the $\overline{\Gamma}$ point)

in the case of K. The calculated energies of the adsorbate localized modes are in agreement with the experimental data obtained for the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na and Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Li superstructures [36, 31]. The energy of the vertical polarized mode localized in the sodium adlayer at the $\overline{K'}$ point, 10.59 meV, is also in agreement with results of Finberg (9.2 meV) [34]. We have also found a similar mode for the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K structure

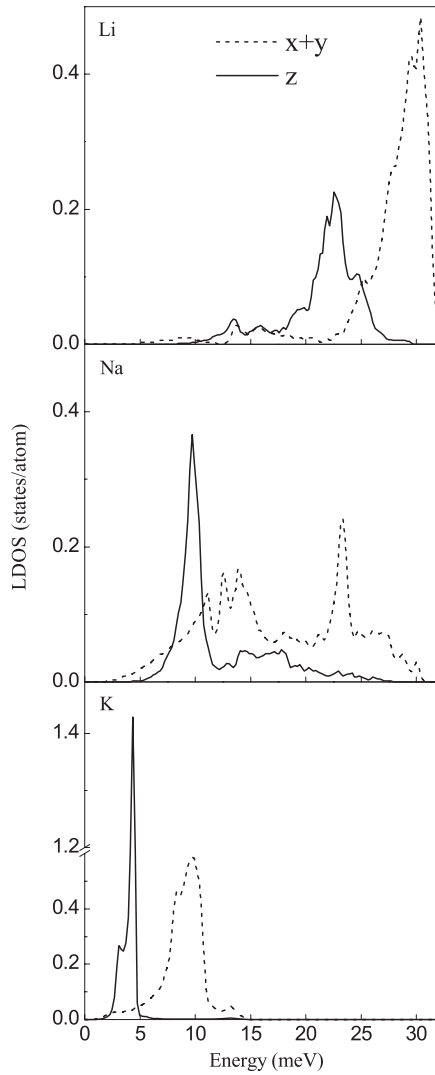


Figure 1. Local density of states of lithium, sodium, and potassium adlayers for Al(111)- $c(\sqrt{3} \times \sqrt{3})$ -AM with AM atoms in substitutional adsorption sites.

that is in agreement with the vertical vibration mode energy obtained experimentally by Finberg *et al* [34]. In figure 1 we show the local densities of states (LDOSs) for alkali adlayers. The analysis of these energies shows that they depend not only on the atomic masses but also on the adsorbate–substrate interactions. The interaction between the adatoms and the nearest-neighbor substrate Al atoms is rather strong for Li and Na. For K, the large distance of adatoms from the substrate results in a much weaker adsorbate–substrate interaction and a stronger interaction between the adatoms than in the previous cases. This agrees well with the electronic structure calculations [29, 47], which indicate a less efficient substrate-mediated screening in the case of K.

In figure 3 we plot the energies of vertical and in-plane polarized modes obtained in EAM calculations as well as the experimental and DFT data as functions of the atomic mass of adsorbates. The linear fit to these data is also plotted. As can be seen in the figure the dependence of the vertical vibration mode energy can be fairly well approximated by a

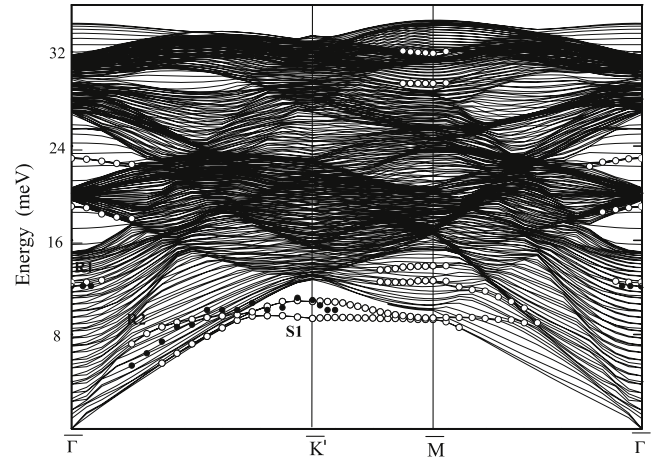


Figure 2. Calculated phonon dispersion curves for Al(111)- $c(\sqrt{3} \times \sqrt{3})$ R30°-Na. The surface states are indicated by open circles. The experimental data from [31] are shown by filled circles.

linear function. Slightly worse fitting is obtained for the in-plane polarized mode. The bigger deviation from linearity for the in-plane mode can be accounted for by distinct in-plane interaction between adsorbates due to the large difference in atomic radii of alkalis. One can note that in systems with alkali atoms in the substitutional position, e.g. in AM/Al(111), the vertical vibration energies are lower than the energies of the in-plane vibrations, while the opposite holds in AM/Cu(001) for the hollow adsorption site. This will be discussed in detail in section 4.

3. Coverage dependence

The dependence of vibrations on alkali coverage was thoroughly studied for the Na/Cu(111) system both experimentally and theoretically. The monolayer saturation occurs at a Na coverage of $\theta \approx 0.44$ (the coverage is defined as a ratio of the number of Na adatoms to the number of Cu surface atoms), when the Na adatoms form a hexagonal ($3/2 \times 3/2$) structure with four atoms per unit cell and with the Na–Na distance close to that in the bulk sodium [3, 48–50]. At low coverages, low-energy electron diffraction (LEED) experiments report either an ordered hexagonal $p(2 \times 2)$ structure at $\theta = 0.25$ [51, 52] or less ordered adsorbate phases up to monolayer saturation [48]. A low-temperature scanning tunneling microscopy (STM) study [50] showed that already at coverages of $\theta \approx 0.11$ (0.25 ML) the Na atoms locally form a $p(3 \times 3)$ hexagonal phase with one atom per unit cell. To describe the transition from the $p(3 \times 3)$ low-coverage structure to the $(3/2 \times 3/2)$ with four atoms per unit cell at the saturated monolayer, Kliewer and Berndt have suggested a model derived from an analysis of the electronic structure of the Na films. This transition includes some intermediate phases, such as a mixing of $p(3 \times 3)$ and $p(2 \times 2)$ structures up to a coverage of $\theta \approx 0.25$ (0.56 ML) and the formation of a $(\sqrt{3} \times \sqrt{3})30^\circ$ structure with three atoms per unit cell at $\theta \approx 0.33$ (0.75 ML). Geometries of the $p(2 \times 2)$ and $(3/2 \times 3/2)$ ordered adsorption

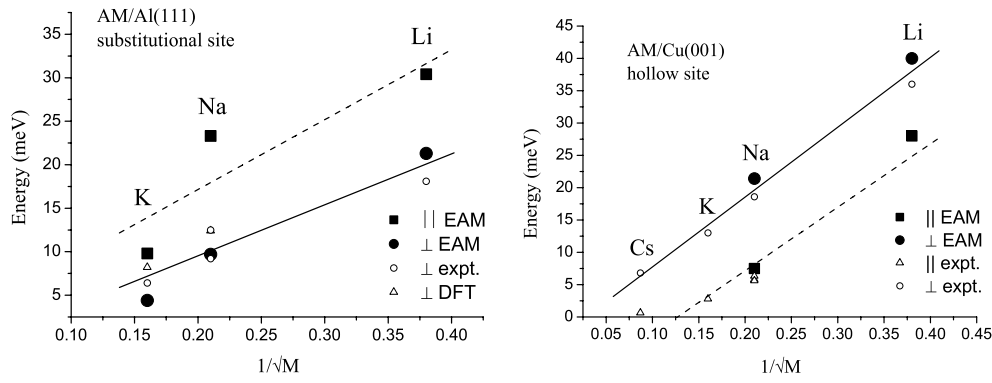


Figure 3. Vibration energy as a function of the inverse square root of the adatoms mass for the substitutional adsorbed AM/Al(111) and for the on-surface adsorbed AM/Cu(001). Solid and dashed lines are linear fits for vertical and in-plane modes, respectively. Computed EAM results for AM/Al(111) are taken from [28] and experimental and DFT data from [31, 34, 36] and [29], respectively. Experimental data for AM/Cu(001) are taken from [56, 58, 59, 78, 80], and [82]. Theoretical data for AM/Cu(001) are the present paper EAM calculation results.

structures on the Cu(111) surface were investigated by comparing the binding energies of the Na adlayer at different high-symmetry sites [9]. It was found that the Na adatoms have a slight preference for adsorption in hollow sites, at least in the case of the $p(2 \times 2)$ structure, in contrast to the heavier alkali metals, which prefer on-top positions [3, 53–55]. For fcc and hcp adsorption positions the obtained values of the binding energy are the same. In the case of the $(3/2 \times 3/2)$ phase the geometry with one sodium atom in the hollow site and three adatoms in distorted hollow sites was found to be preferable [9].

As for the vibrational properties, the phonon dispersion curves have been measured using He scattering [30, 56] for Na films on Cu(001) made of 1–30 ML, and then analyzed within the framework of a force constant model [57]. For Na atoms adsorbed on the Cu(111) surface, the frequency and the intensity of adatom–substrate stretch vibrations have been measured using electron-energy-loss spectroscopy (EELS) [27, 58–60]. The vibrational energy of the stretching (S) mode was found to be of ≈ 21 meV and almost independent of the coverage within the range of 0–0.35 ML, whereas the intensity appeared to be strongly coverage dependent, with a maximum at about 0.15 ML. In *ab initio* calculations of a monolayer Na film on Cu(111) [61], the adatom–substrate stretch energy of 21 meV was obtained from the curvature of the total energy with respect to the displacement of a rigid adlayer placed on a rigid substrate. The results of a detailed comparative theoretical study of the equilibrium crystal structure and vibrational properties of the Na/Cu(111) system at coverages up to the monolayer saturation have recently been presented in [32]. The ordered structures: $p(3 \times 3)$, $p(2 \times 2)$, $(\sqrt{3} \times \sqrt{3})30^\circ$, and $(3/2 \times 3/2)$ were considered. It was found that all the surface modes inherent to the clean Cu(111) surface remain at any coverage. They show a mixing character coupling to the adsorbate modes. This coupling leads to small alterations of their frequencies. The mode associated with the adatom–substrate stretch vibrations was obtained to be at ≈ 22 meV for all the structures considered (see figure 4). The calculated vibrational energy agrees well with the value of 21 meV measured by EELS and found to be almost constant for

any submonolayer coverage [60]. At the saturated monolayer many maxima appear in LDOS for z -polarized vibrations of adatoms, making the LDOS much broader compared to that for lower coverages. One of these maxima corresponding to the vibrations of adsorbates in the hollow positions remains at about 22 meV. The sodium atoms located in the distorted hollow sites interact more strongly with the substrate due to the shorter Na–Cu distances and as a result have higher vibrational energies. Two adlayer in-plane polarized modes are located below the bottom of the Cu bulk phonons for the $p(3 \times 3)$ and $p(2 \times 2)$ structures. As regards their energies, they show an upward shift with increasing coverage. The ‘splitting’ of these in-plane vibration modes is caused by the hybridization with the substrate acoustic modes. When they fall outside the Cu bulk continuum, they become almost degenerate. These modes appear in the corresponding LDOSs as a narrow prominent peak. In the $(\sqrt{3} \times \sqrt{3})$ and $(3/2 \times 3/2)$ structures these modes are shifted towards higher energies above the bulk phonon edge. So, unlike the z -polarized surface resonance at the $\bar{\Gamma}$ point (the stretch S mode), the vibrational energy of the in-plane polarized modes is found to be strongly coverage dependent. It increases by a factor of three with the increasing coverage from $\theta \approx 0.11$ to $\theta \approx 0.44$. This dependence is due to the fact that the distance between adatoms becomes shorter with the increasing coverage and, as a result, the interaction in the adlayer film becomes stronger too.

The same tendency was found in K/Pt(111), see figure 5. Vibrations of the K/Pt(111) system have been measured using electron-energy-loss spectroscopy (EELS) [62] and scanning tunneling microscopy (STM) [63] as a function of the K coverage at room temperature. It was shown [62] that the K adsorption induces a single loss peak of the K vibration normal to the surface, the energy of which increases at low K coverages (16.91 meV at $\theta_K = 0.02$ ML), then passes through a maximum (21.7 meV at $\theta_K = 0.16$ ML) and decreases linearly at higher coverages (19.22 meV at $\theta_K = 0.33$ ML). In a recent experimental work the K-covered Pt(111) surfaces have been studied in the coverage range from 0.23 to 0.61 ML by using femtosecond time resolved second-harmonic generation spectroscopy (TRSHG) [64]. For coverages θ

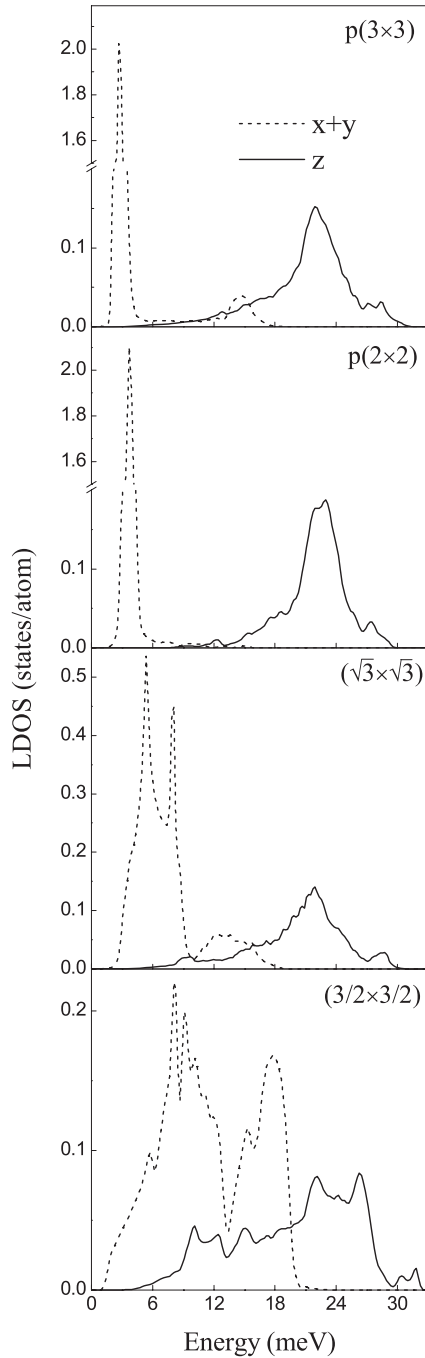


Figure 4. Local density of states of sodium adlayer for Cu(111)-p(3 × 3)-Na, Cu(111)-p(2 × 2)-Na, Cu(111)-($\sqrt{3} \times \sqrt{3}$)-Na, and Cu(111)-(3/2 × 3/2)-Na with Na atom in hollow adsorption site.

between 0.34 and 0.38 ML the K–Pt stretch mode was found to be 19.44 meV. At lower coverages Fuyuki *et al* observed two peaks with close energies (19.44 and 21.92 meV). This was attributed to the coexistence of p(2 × 2) and ($\sqrt{3} \times \sqrt{3}$)30° domains.

In our calculations of vibrational properties of the Pt(111)-p(2 × 2)-K and Pt(111)-($\sqrt{3} \times \sqrt{3}$)30°-K systems the mode associated with the adatom–substrate stretch vibration was obtained at ≈ 20 meV for both structures considered

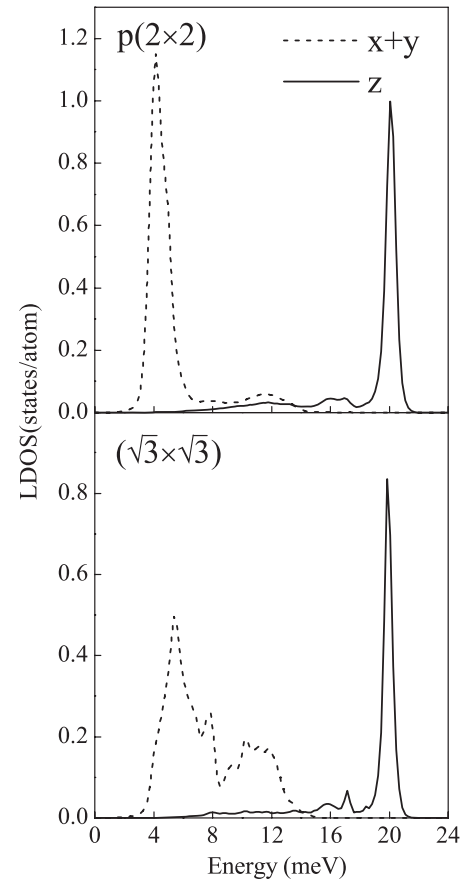


Figure 5. Local density of states of potassium adlayer for Pt(111)-p(2 × 2)-K and Pt(111)-($\sqrt{3} \times \sqrt{3}$)-K with K atom in hollow adsorption site.

(figure 5). This vibrational energy agrees well with the value of 19.22 meV measured by EELS [62] and the computational result of Moré *et al* [65] (19.09 meV). Like the case of Na/Cu(111), the intensity of the z-polarized mode decreases with increasing coverage from 0.25 to 0.33 ML, that is also in agreement with the experiment [62]. Two adlayer in-plane polarized modes are located below the bottom of the Pt bulk phonons for both structures. These modes appear in the corresponding LDOSs as peaks at 4.1 and 5.4 meV for the p(2 × 2) and ($\sqrt{3} \times \sqrt{3}$)30° structures, respectively. The energies of the in-plane modes are shifted towards higher energies with the increasing coverage, similar to the case Na/Cu(111). For both structures considered the vertical vibration mode produces a very small width of the LDOS peak that corresponds to a weak interaction of potassium with the Pt substrate. The in-plane vibration peak width in the case of Pt(111)-($\sqrt{3} \times \sqrt{3}$)30°-K is substantially broader than that for the Pt(111)-p(2 × 2)-K system, which reflects the enhancement of the lateral K–K interaction with the coverage growth.

4. Dependence on adsorption position

Various experimental studies (see, for instance, Finberg *et al* [34] and references therein) indicate that the adsorption sites play an important role in vibrations of alkali atoms on metal

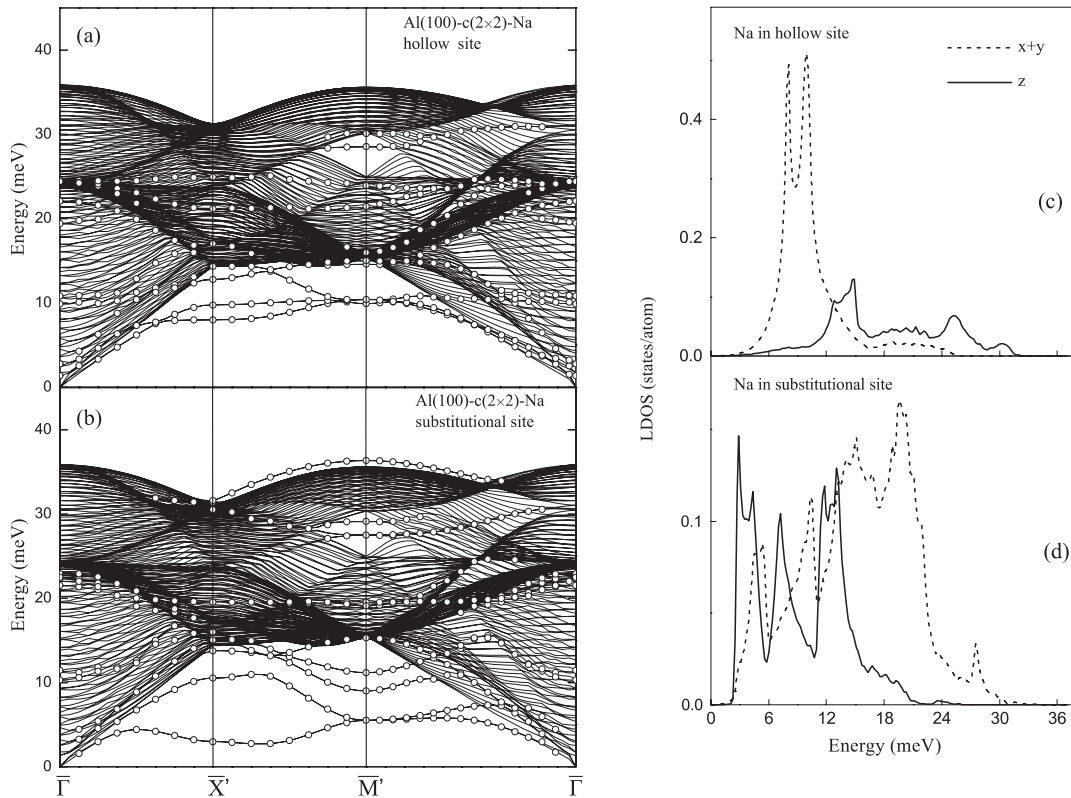


Figure 6. Phonon dispersion curves and LDOS for Al(001)-c(2 × 2)-Na with sodium atoms in hollow ((a) and (c)) and in substitutional ((b) and (d)) adsorption sites (surface states are denoted by open circles).

surfaces. For instance, the z -polarized mode energies observed for alkalis in substitutional adsorption sites are very distinct from those found for alkalis in top or hollow sites. This conclusion, resulting from analysis of HAS and HREELS data for alkalis on distinct metal substrates, carries information about the joint effect of the adsorption site and the substrate. Here we clarify this point, carrying out the analysis of vibrations for Na atoms located in different adsorption sites on the same surface, Al(001) [66]. In figure 6 we show the calculated phonon dispersion and LDOS [66] for the Al(001)-c(2 × 2)-Na surface structure formed by the adsorption of $\frac{1}{2}$ ML of Na atoms in hollow and substitutional sites (low temperature and room temperature crystal structures, respectively [67–72]). The reason why Na atoms occupy the hollow sites at low temperature and substitutional sites at room temperature is that at room temperature the adsorption process involves a temperature-activated vacancy formation on the surface, and the adsorbate atoms occupy these vacancies to form an ordered substitutional structure. The same structure also occurs if the adatoms are adsorbed at low temperature and the substrate subsequently is heated to room temperature [3]. This transition is irreversible, indicating that the low temperature structure is metastable. Since for the Al(001)-c(2 × 2)-Na phase the experimental data on the vibrational modes of Na are not available, we discuss the dependence of adatom vibrations using phonon spectra shown in figure 6.

As follows from figure 6(a), the Na adsorption in hollow sites gives rise to two low-energy surface modes below the bottom of the bulk spectrum of Al. These frustrated translation

modes are associated with the in-plane displacements of the Na adsorbates. At the \bar{X}' point their energies are 7.98 and 9.76 meV. These modes produce the main contribution to the in-plane adsorbate motion and appear in the corresponding LDOS as the most prominent feature, a double low-energy peak. The upper T mode couples to the substrate acoustic shear-vertical (z -polarized) mode [66]. Similar T modes with a negligible dispersion and strong coverage dependence were also obtained for Na adsorbates on the Cu(001) and Cu(111) substrates [28, 35]. Another adsorbate-induced vibrational mode in the Al(001)-c(2 × 2)-Na system was obtained at energy of 19.44 meV at the $\bar{\Gamma}$ point. This resonance associated with adatom–substrate stretch vibration exists only at small wavevectors near the BZ center. At higher energies, 21–25 meV, two wide surface resonances appear. The upper resonance mode also exists at clean Al(001) near the BZ center and is mainly determined by the vertical motion of the subsurface Al atoms. Upon Na adsorption, this mode couples to the adsorbate atom motion along the surface normal and spreads over the entire BZ. The lower-energy surface resonance is mainly determined by the in-plane motion of Na adatoms. Vibrational energies of these resonances depend slightly on wavevectors, except that the lower resonance shows a small dispersion on moving to the zone center. As regards the substrate vibrations, most of the clean surface modes including the Rayleigh wave mode remain. The presence of adsorbates leads to an alteration of their frequencies and to mixing with the adsorbate atom motion.

The phonon dispersion curves for Al(001)-c(2 × 2)-Na with sodium in substitutional positions are shown in figure 6(b). In this case the mode associated with the adatom–substrate stretch vibration appears at lower energies, 11.46 meV at the $\bar{\Gamma}$ point. Another resonance mode which lies just above the first one is mainly characterized by shear-horizontal displacements of adatoms. As in the case of hollow site adsorption, two low-energy modes appear below the bulk Al phonon spectrum, but now these modes are characterized by displacements of adsorbates and the top-layer Al atoms in mutually perpendicular directions. The upper of these two modes is mainly associated with the in-plane displacements of adatoms and involves the vertical motion of the top substrate atoms. The lower one is mainly characterized by the adlayer atom motion in the direction perpendicular to the surface. Unlike the case of hollow site adsorption, a new substrate surface mode is found above the bulk Al phonon spectrum. It is determined by the vertical motion of the substrate atoms in the first and the third layers as well as by the in-plane displacements of Al atoms in the second layer. Such a mode splitting above the bulk phonons is a typical feature for the case of a large surface relaxation and a substantial increase of surface–subsurface interlayer interactions [73]. The calculation also shows that the Na–Na interactions are not weak, in contrast to the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Na system, where they are well screened by the surface electron density. This is a reason for the more complicated phonon spectra in comparison with weak dispersed states in Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Na, that give narrow peaks of LDOS. In general, comparing phonon spectra shown in figures 6(a) and (b), one can clearly see that the change of the adsorption site from the hollow to the substitutional one results in a strong modification of both vertical and in-plane vibration spectra.

5. Surface orientation effect

As follows from table 1, the vibrational data, both experimental and theoretical, for the Li, Na, K, and Cs adsorbates (adlayers) are available for all low-index surfaces of copper. We use these data here to analyze the effect of surface orientation on alkali adatom vibrations.

In early works of Rudolf, Astaldi, and Modesti [58, 59, 74], a weak dependence of the AM–Cu stretch vibration mode on the substrate surface orientation was found. Thus, the vertical vibration energy of Li on the low-index Cu surfaces was estimated to be 35–37 meV. The frequency of the adsorbate–substrate stretch mode in the case of sodium was found to be ≈ 18 meV for all surface orientations studied. On the Cu(110) surface Rudolf *et al* found an additional energy loss peak at 11.5 meV, which was attributed to a reconstruction effect of the surface under sodium adsorption. Similar results were obtained for potassium, with the only difference that the energy of the vertical vibration of a K adlayer on Cu(110) was found to be 14 meV in the unreconstructed case, that is somewhat higher than for (111) and (001) surfaces, where it was estimated as 12 meV. As in the case of sodium, an additional mode at 10 meV was also observed on a reconstructed Cu(110) surface. Later, Lindgren *et al* [60, 75] investigated vibrations in

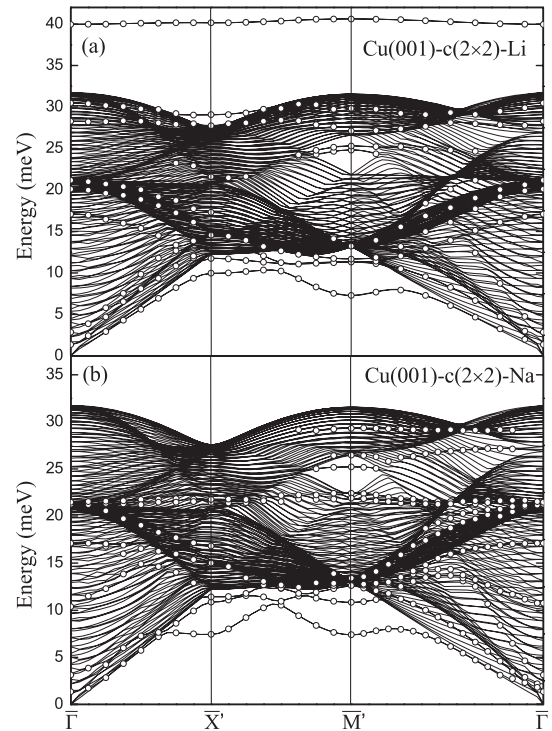


Figure 7. Phonon dispersion curves for Cu(001)-c(2 × 2)–AM with lithium (a) and sodium (b) adatoms in hollow adsorption sites (surface states are denoted by open circles).

Li, Na, and K adlayers on Cu(111). The measured vibration energies of 43, 21, and 13 meV, respectively, are slightly higher than those reported in [58, 59, 74]. In *ab initio* calculations of a Na monolayer on Cu(111) [61] the adatom–substrate stretch energy of 21 meV was obtained. For this mode an energy of ≈ 22 meV was also obtained from EAM calculations [32]. The calculation of phonon spectra of Li/Cu(001) and Na/Cu(001) systems revealed the energies associated with the adsorbate–substrate stretch mode at 40.0 and 21.4 meV (almost dispersionless bands in the whole BZ in figure 7), respectively. The latter value is slightly higher than the monolayer frequency estimated by fitting from the HAS measurement data for multilayer films of sodium on Cu(001) [30]. From all these results it is difficult to see any significant effect of the Cu surface orientation on the Li and Na atom vibrations. Taking into account available data for vibrations in a K adlayer on different copper surfaces one can conclude that no dependence of vertical vibration energy is found either. This can be attributed to the large atomic radius of potassium that makes K–Cu bonding less dependent on the geometry of the substrate. The same is observed for the stretch mode of Cs on Cu surfaces. The frequency of the Cs monolayer on Cu(001) was determined from the fit of HAS data as 5.4 ± 0.5 meV [56]. The vertical vibration energy of Cs on Cu(111) extracted from [76] is approximately equal to 5 meV.

On the other hand, the comparative study [77] of ordered structures Al(111)-($\sqrt{3} \times \sqrt{3}$) and Al(001)-c(2 × 2) formed by sodium in a substitutional position and the analysis of the corresponding force constants revealed that the interaction between adsorbates and nearest-neighbor substrate atoms

depends on a surface structure. For Al(111)-($\sqrt{3} \times \sqrt{3}$)-Na this interaction is rather strong while Na-Na interaction in this system is very weak. In Al(001)-c(2×2)-Na the Na-Al interaction is weaker than that in the previous case, while Na-Na bonding is quite strong. In particular, this gives rise to the shear-horizontal and longitudinal adlayer localized modes and leads to more complicated sodium vibrations in the Al(001)-c(2×2)-Na system (compare figures 1, 2 and 6).

Summarizing the results given in the present section one can conclude that, in general, the surface substrate orientation can strongly influence the stretch and frustrated translation modes of the adsorbed alkali atoms.

6. Conclusions

We have presented calculations of the local density of vibrational states for Pt(111)-($\sqrt{3} \times \sqrt{3}$)-K, Pt(111)-c(2×2)-K, Cu(001)-c(2×2)-Li, and Cu(001)-c(2×2)-Na. Based on these and earlier published experimental and theoretical results we discussed the dependence of both stretch (z -polarized) and frustrated translation (in-plane polarized) modes on atomic mass, adsorption position and coverage of alkali atoms. We also discussed the dependence of vibrational energies on the substrate orientation. The following conclusions have been drawn. (1) The atomic mass square root dependence of the stretch mode energy has been confirmed by using the Al(111) and Cu(001) substrates as examples. It was shown that the frustrated translation mode also follows this dependence, however, with worse accuracy. (2) We have confirmed that in a wide range of submonolayer coverages the stretch mode energy remains nearly constant. In contrast, the in-plane polarized modes vary with the coverage: the vibration energy increases with the increase of alkali coverage. (3) We have shown that the spectrum of both stretch and frustrated translation vibrations can be very sensitive to the adsorption position of alkali atoms. (4) The alkali atom vibrations on metal substrates can be strongly influenced by the substrate orientation.

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