Antiabsorption Resonances in Infrared Reflectance Spectroscopy of Alkali-Cu(111) Adsorbate Systems: Is the Ground State a Surface Charge Density Wave Condensate?

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We have observed antiabsorption resonances when alkali metals are adsorbed on Cu(111). The resonances occur at $\hbar \omega_0 \approx 0.1$ eV and cannot be attributed to phonon modes. We show that the experimental data can be consistently explained by attributing the resonances to vibrations, parallel to the surface, of a pinned surface charge density wave (CDW). We estimate the CDW effective mass to be m^* $\approx 500 m_e$ per electron in the condensate.

The recent observation of antiabsorption resonances in infrared reflection absorption spectroscopy (IRAS) has stimulated interest in understanding the nature of these resonances [1,2]. Using synchrotron radiation such resonances have been observed for the external vibrations of CO adsorbed on Cu(100) and Cu(111) [1]. IRAS measurements revealed two bands in the far infrared, an absorption band due to the Cu-CO stretch mode at 345 cm^{-1} and an antiabsorption band with a Fano-like line shape at 285 cm^{-1} assigned to the frustrated rotation (bending motion) of the molecule. Since the latter mode is dipole forbidden with respect to an electric field normal to the surface, it should not be observed according to the surface dipole selection rule. Recently, Persson and Volokitin [2] proposed a mechanism for this antiabsorption resonance, which is based on the *surface resistivity* the conduction electrons encounter. Scattering of the electrons from the adsorbed molecules then results in a broadband absorption of the ir light. When the ir frequency coincides with the resonance frequency of the parallel adsorbate vibrations, the molecules move in resonance with the collective drift motion of the electrons; hence the additional surface resistivity vanishes and the ir reflectivity approaches the original value of the clean surface. This results in an antiabsorption peak which is observed at the frequency of the molecular vibration parallel to the surface (frustrated rotation or translation). In the present work we report the first observation of a novel antiabsorption resonance for K and Na layers adsorbed on Cu(111), and which we believe *does not originate from a vibrational mode of the adsorbed atom*, but rather from the vibrations, parallel to the surface, of a pinned surface charge density wave.

The experiments were performed at the U4-IR beam line at the National Synchrotron Light Source at Brookhaven National Laboratory [3]. Infrared radiation in the spectral range from 150 to 2500 cm^{-1} was focused using $f/10$ optics at an angle of incidence of 87° onto the copper single crystal. The spectra reported here were ob-

tained at a resolution of 6 cm^{-1} by coadding 256 scans in a total measurement time of 100 s. The Cu samples were prepared by mechanical polishing ending with a 0.3 µm cerium oxide polishing compound. In UHV, the sample was cleaned by Ne$^+$ sputtering at 500 K with a subsequent anneal to 900 K. Potassium layers were prepared by evaporation from a SAES getter source and characterized following experimental procedures described earlier [4,5].

Time-evolved infrared spectra obtained during evaporation of potassium on a Cu(111) surface at 92 K are shown in Fig. 1. The spectra were collected at time intervals of 100 s, and characterize the growth of a potassium
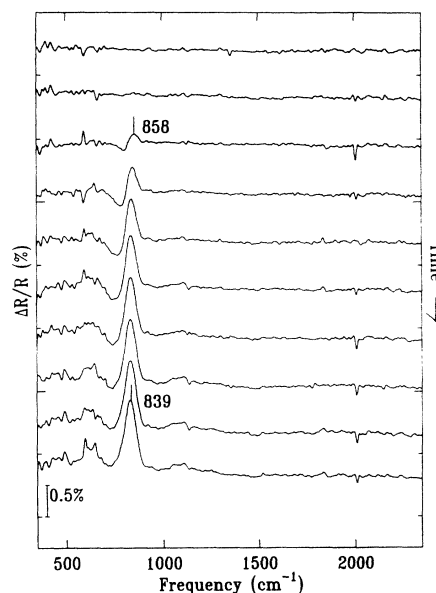

FIG. 1. Time-resolved infrared spectra obtained during deposition of potassium on Cu(111) at 92 K ($\theta_K = 0.66$, or 1.64 ML). The spectra show a strong antiabsorption feature at ≈ 850 cm^{-1}. The time interval between the spectra is 100 s.

layer with a final coverage of $\theta_K = 0.66$ (1.64 ML). Most noticeable is the evolution of a strong antiabsorption resonance at 850 cm^{-1}, which exhibits a strong derivativelike line shape at low coverage ($\theta_K \approx 0.20$). (Note that conventional absorption features in these spectra would show up as dips or minima in Fig. 1.) At the highest coverage shown, the line shape has evolved into an antiabsorption band with a FWHM of 75 cm^{-1}. The frequency of the peak maximum of this band exhibits only a weak coverage dependence by shifting from 858 cm^{-1} at low coverage to 839 cm^{-1} at the highest coverage shown in Fig. 1. The intensity of this band shows a characteristic *nonlinear coverage behavior* as shown in Fig. 2. The antiabsorption band does not appear until $\theta_K \approx 0.20$, a coverage which corresponds to the minimum of the work function curve [6], and saturates with completion of the monolayer at $\theta_K \approx 0.40$. Experiments with alkali layers up to 5 ML reveal no further change in intensity. This suggests that the *antiabsorption resonance is related to the metallic state of the potassium monolayer in contact with the Cu(111) surface.* In fact, reaction of a K/Cu(111) layer with oxygen results in complete quenching of the antiabsorption resonance (not shown here). Previous studies have shown that alkali atoms form strong compounds with oxygen resulting in a largely ionic species, e.g., potassium superoxide [5]. Since the K-4s electron is largely involved in the reaction, the metalliclike behavior of the alkali is lost in the process. We also note that the antiabsorption resonances disappeared when the crystal was heated above 200 K.

The high frequency of the band at 850 cm^{-1} suggests that the *antiabsorption resonance does not originate from a vibrational excitation*, since the K-Cu vibration is to be expected at 150 cm^{-1} in analogy with other K-metal vi-
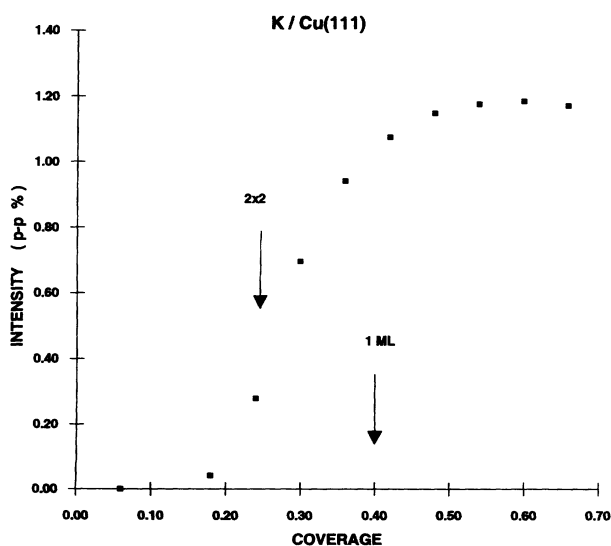
brations [4]. This point is conclusively demonstrated by the fact that the resonance is observed at the same frequency for a Na layer adsorbed on Cu(111). Figure 3 shows a comparison of the infrared spectra obtained for a K layer (a) and a Na layer (b) adsorbed on Cu(111) at 92 K. The Na layer exhibits a resonance at 835 cm^{-1}, and a line shape which is very similar to that of the K layer. The similarity in the frequency is a clear indication that the observed antiabsorption resonance is not due to a vibration of the alkali metal, but *must be rather related to the Cu(111) substrate*. In fact, no antiabsorption band is observed for the Cu(100) surface, as shown in Fig. 3, spectrum (c) for a Na layer.

A theory has recently been developed which predicts that parallel adsorbate vibrations should result in antiabsorption resonances in IRAS. It is clear that the resonance structures in Figs. 1 and 3 cannot result from coupling to the adsorbate or substrate vibrations since the highest phonon frequency in bulk copper is only ≈ 300 cm^{-1} and the alkali-induced vibrations occur at even lower frequencies. Hence one may ask if there exist other types of excitations which couple to an external ir light beam in a similar way as parallel adsorbate vibrations. We have found only one such case, namely, vibrations of a *pinned surface charge density wave (CDW)*.

Associated with a surface CDW [7–10] is a modulation of the electron charge density which in the simplest case may take the form $\sim\cos(2k_0x+\varphi)\exp(-\gamma z)$, where the positive z axis points into the substrate. We assume that the surface CDW is pinned by surface imperfections (e.g., steps) or by lattice commensurability.

FIG. 2. Coverage dependence of the peak-to-peak intensity of the antiabsorption resonance at 850 cm^{-1} for K/Cu(111).
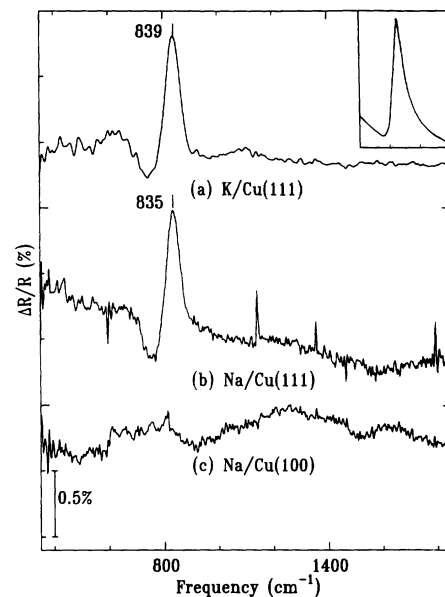

FIG. 3. Infrared spectrum for three different systems: (a) K/Cu(111), (b) Na/Cu(111), and (c) Na/Cu(100). The inset shows the theoretical calculated antiabsorption peak for ω_0 = 835 cm^{-1} and η = 75 cm^{-1} (note ω_1 = 500 cm^{-1} for copper).

Let n_s be the number of electrons per unit area in the surface CDW condensate. The effective mass m^* of the condensate electrons and n_s are assumed to be intrinsic properties of the unpinned surface CDW in the absence of an applied electric field. The equation of motion governing the parallel displacement $q(t)$ of the surface CDW from its equilibrium position is assumed to be

$$\ddot{q} + \eta(\dot{q} - v) + \omega_0^2 q = eE/m^* . \qquad (1)$$

Here ω_0 is the pinning frequency and v the drift velocity (induced by the electric field E) of the "normal" electrons just below the surface. Note that the friction force $F = -m^*\eta(dq/dt - v)$ depends on the relative velocity of the charge density wave and the drift velocity of the normal electrons. The power absorption induced by the surface CDW is

$$P = n_s A\langle(v - \dot{q})F\rangle = n_s A m^* \eta\langle(v - \dot{q})^2\rangle , \qquad (2)$$

where A is the surface area and $\langle \cdots \rangle$ stands for the time average. To linear order in n_s we can calculate P by using the drift velocity v for the normal electrons obtained without a surface CDW. The change in the ir reflectivity induced by this surface CDW is given by $\Delta R = -P/I_0 A_0$, where A_0 is the cross-section area of the incident photon beam. The surface area A covered by the incident beam is $A = A_0/\cos\theta$, where θ is the angle of incidence. The intensity of the incident ir beam is determined by the pointing vector and is given by $I_0 = cE_0^2/8\pi$, where E_0 is the amplitude of the electric field of the incident light beam. Using these equations together with (1) and (2) and the Fresnel formulas for the electric field in the metal gives

$$\Delta R = -\frac{4}{c}\frac{n_s}{n}\frac{m^*}{m}\frac{\eta}{\cos\theta}\frac{(\omega_0^2 - \omega^2)^2}{(\omega_0^2 - \omega^2)^2 + \omega^2\eta^2} . \qquad (3)$$

This formula predicts an enhanced reflectivity at resonance, $\omega = \omega_0$, and that the full width at half maximum (FWHM) of the reflectivity peak equals η.

Let us apply (3) to the alkali-copper adsorption systems. First, note that alkali-induced antiabsorption resonances occur for both K and Na on Cu(111) but not on Cu(100). Now, the important difference between these two surfaces is that for Cu(111) an occupied (alkali-derived) state occurs in the projected bulk band gap both for Na [11] and K [12], but no such state is found for Cu(100) since this surface has no projected bulk band gap below the Fermi level. Hence we postulate that for an alkali-covered Cu(111) surface this state has undergone a charge density wave condensation [13]. The number of electrons per unit area in this state is $n_s \approx k_0^2/2\pi$, where $k_0 \approx 0.2$ Å^{-1}. The "height" of the antiabsorption peak tends to saturate at about 0.012 at "high" alkali coverage ($\theta > 0.5$; see Fig. 2), and assuming that in this limit all the electrons in this state occur in the CDW condensate, (3) gives $m^* \approx 500$ m. In this calculation we have used $\theta = 87°$ and the damping $\eta = 75$ cm^{-1} from the width of the antiabsorption resonances in Figs. 1 and 3.

We now present a number of further observations which support this model of a surface CDW condensate on the alkali-covered Cu(111) surface.

(1) Antiabsorption peaks are observed only for the range of alkali coverage where the alkali layer is in a metallized state [15]; see Figs. 1 and 2. If a surface CDW condensate existed on the clean Cu(111) surface, the associated electric field lines would extend out on the vacuum side of the surface and contain field energy. This would tend to destabilize the CDW state and probably make the "normal" metallic state have lower energy. A conducting "alkali slab" on the Cu(111) surface, on the other hand, will screen out the electric field and hence stabilize the CDW state. Indeed, we have proven that the antiabsorption resonances start to occur exactly when the alkali layer "metallizes": By exposing the surface first to CO and then to the alkali metal, we found that the intensity of the C-O stretch vibration disappears due to screening in the same narrow alkali coverage range where the antiabsorption peak starts to appear. Furthermore, if the alkali layer is oxidized (by exposure to oxygen), the antiabsorption peaks disappear as expected because alkali oxides are insulators and cannot screen out the electric field lines on the vacuum side of a CDW.

(2) In Fig. 1 weak structures occur at both lower and higher frequencies than the dominant peak at $\hbar\omega_0 \approx 0.1$ eV. We interpret the main peak as originating from a dominant type of surface pinning centers, e.g., steps, and the weaker structures as associated with a wide distribution of other types of pinning centers. The intensities of these other structures were found to vary strongly with sample preparation (e.g., annealing). Furthermore, with a very high quality, electropolished crystal no antiabsorption structures were observed for $\omega > 350$ cm^{-1} (with the possible exception of very weak bands). This is attributed to the absence of "strong" pinning centers. On this surface no antiabsorption structures were observed even after extensive sputtering, indicating that local defects made this way do not create the required pinning centers. This variation in the frequency dependent transport properties with sample quality is one of the most characteristic properties of CDW systems [7].

(3) The shapes and width of the antiabsorption resonances for the K-Cu(111) and Na-Cu(111) systems are almost identical. Furthermore, the resonance frequency varies from 858 to 839 cm^{-1} with increasing K coverage, and from 846 to 835 cm^{-1} with increasing Na coverage; i.e., the resonance frequency is practically independent of both the coverage and type of the alkali metal. This is exactly what one would expect if the main effect of the alkali layers is to screen out the electric field of the surface CDW on the vacuum side, and if the CDW is mainly localized to the copper crystal and determined by the intrinsic properties of copper.

(4) The antiabsorption structures in Fig. 3 are slightly asymmetric with a higher reflectivity on the high-frequency side. This effect is predicted by a more accurate

theory [16], which accounts for the nonlocal dielectric properties of copper (related to the anomalous skin effect). This theory predicts a unique shape of the antiabsorption resonance which only depends on the ratio ω_0/ω_1, where $\omega_1 = \omega_p v_F/c \approx 500$ cm^{-1} for copper (ω_p is the plasma frequency and v_F the Fermi velocity). For $\omega_0/\omega_1 \gg 1$ Eq. (3) is obtained and the antiabsorption resonance is a perfect Lorentzian, while the resonance becomes more and more asymmetric as ω_0/ω_1 decreases. For $\omega_0 = 840$ cm^{-1} and hence $\omega_0/\omega_1 \approx 1.7$, the inset in Fig. 3 shows the theoretically predicted line shape.

It is worth noting the fact that the antiabsorption resonance is coupled to the electric field *parallel* to the surface. This means that even though it is observed with IRAS, it might not be detectable with electron energy loss spectroscopy (EELS). As recently pointed out [2], for $\hbar\omega \sim 0.1$ eV the ratio between the parallel and the normal electric field inside the metal surface is about 2 orders of magnitude larger in IRAS than in EELS, making it unlikely that these resonances could be observed with EELS.

Finally, it is interesting to note that in two recent STM studies from clean Cu(111) and Au(111) surfaces, periodic charge density oscillations parallel to the surface have been observed with the wavelength $\sim 2\pi/2k_0 \sim 15$ Å [17,18]. But these oscillations seem to be associated with Friedel oscillations in the surface state charge density, rather than with a surface CDW condensate [19].

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[19] Friedel oscillations parallel to the surface give rise to an effective "corrugated" surface potential, which in principle could scatter the copper conduction electrons and contribute to a background absorption in ir spectroscopy. In order to give rise to an antiabsorption resonance at around 800 cm^{-1} it must be possible for the Friedel oscillations to oscillate (in time) parallel to the surface with this characteristic frequency; as far as we know there is no theoretical work which suggests that such an excitation may exist.