

STUDIES OF ALKALI ADSORPTION ON Rh(111) USING OPTICAL SECOND-HARMONIC GENERATION

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Dramatic changes were observed in the optical second-harmonic generation from the Rh(111) crystal surface as the surface was covered with alkali atoms. For low alkali coverage, these changes are explained qualitatively in terms of optical transitions between alkali atomic-derived electronic states and, for high coverage, in terms of the plasmon resonance of the alkali layer. The results establish the surface specificity of second-harmonic generation to the topmost 1 or 2 atomic layers of alkali metals.

1. Introduction

Optical second-harmonic generation (SHG) has recently been demonstrated to be an effective tool for surface studies [1]. It has enough sensitivity to detect a submonolayer of adsorbate on a substrate [2]. In a recent experiment, the technique was used to study submonolayers of atomic and diatomic adsorbates on a Rh(111) surface in ultrahigh vacuum [3]. It was found that upon adsorption of CO and O, the SH signal from the Rh(111) surface decreased. The result can be explained in a simple physical way: CO and O are electron acceptors; upon adsorption, they partially localize the nearly free electrons on the metal surface. Since the optical nonlinearity of a metal surface can be largely accounted for by the nearly free electrons [4], it is expected to be reduced by the localization of such electrons. This being the case, one should find an increase in surface nonlinearity if electron donors are adsorbed on a metal surface.

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In this paper, we report that, when alkali atoms are adsorbed on Rh(111), the SH signal from Rh(111) increases drastically. Our results indicate, however, that the very large increase in surface nonlinearity due to adsorption of alkali atoms cannot be explained simply by the increase in the number of nearly free electrons in the metal, but is most likely the consequence of a significant modification of the optical transitions between alkali-derived states resulting from a relative shift of the Fermi level. SHG is such a sensitive surface probe that adsorption of less than 1% of a monolayer of alkali atoms on Rh can be easily detected. Similar SH intensity was observed for Na overlayers on Ge [5] and Cu [6] by Chen et al. The adsorption of alkali atoms on transition metals is of great importance. The alkalis are known to be promoters for certain catalytic processes [7], e.g., the dissociation of CO and N₂ for hydrocarbon and ammonia synthesis, respectively.

2. Experiments

Our experiments were conducted in an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. The Rh(111) surface was cleaned with cycles

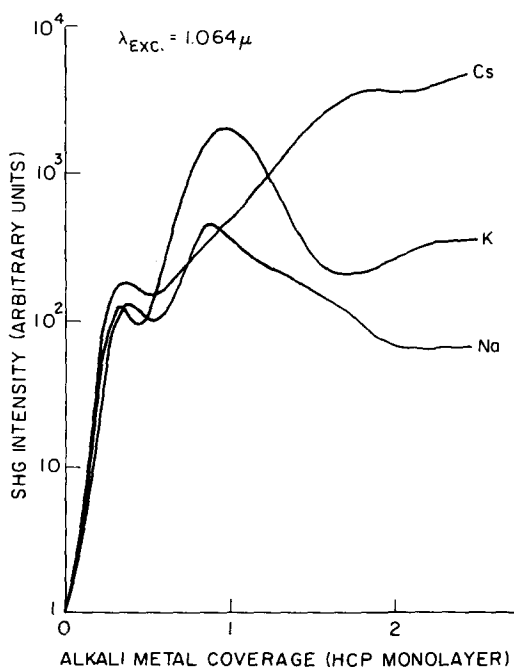


Fig. 1. Second harmonic output as a function of alkali metal coverage for Na, K, and Cs on Rh(111) with 1.06 μm laser excitation.

of Ar^+ sputtering, heating at 1000 K in 2×10^{-7} Torr of O_2 , annealing at 1200 K in vacuum, and then flash heating to 1300 K. The cleanliness and order of the surface were checked with Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The sample was flash-heated again to 1300 K just before alkali-dosing to remove possible surface contaminants like CO adsorbed from the background and C and O deposited by the dissociation of CO during the AES probing. SAES getters were used as the alkali sources. They were mounted in such a way that SHG from Rh(111) could be monitored during alkali dosing and the dosage rate could be simultaneously detected by a quadrupole mass spectrometer.

For the SH measurements, Nd : YAG laser pulses at 1.06 or 0.532 μm with ≈ 7 ns pulsewidth and 6 mJ pulse energy were \hat{p} -polarized and incident on the Rh sample at an angle of 67.5° with a beam diameter of 1 mm. At this intensity, no laser-induced desorption or surface damage could be detected. The SH radiation from the surface was \hat{p} -polarized, and was detected after proper filtering by a photomultiplier in conjunction with a gated integrator system. The SH signal generated from the clean Rh surface was fairly strong, about 10^3 photons/pulse. With the 10 Hz repetition rate of the laser, the measurements were accurate to $\pm 5\%$ using a 1 s time constant. The results

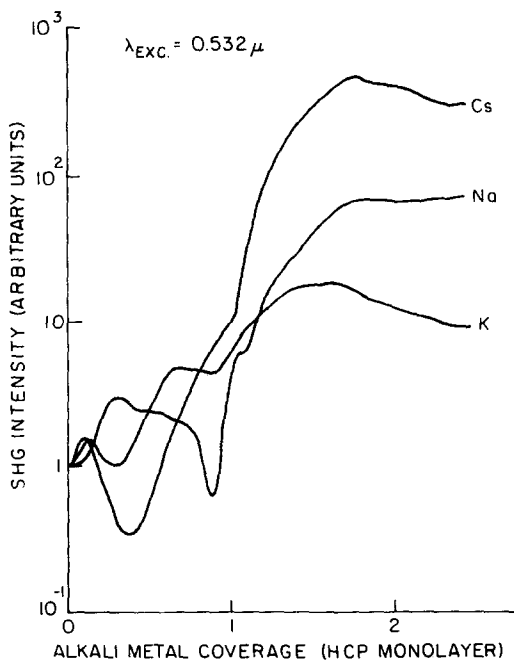


Fig. 2. Second harmonic output as a function of alkali metal coverage for Na, K, and Cs on Rh(111) with 0.53 μm laser excitation.

presented in figs. 1 and 2 were obtained by monitoring SHG from the surface as continuous functions of time during the alkali atom doses at ≈ 1 monolayer/min, but were converted to functions of alkali coverage using the measured dosing rates and calibrating with LEED.

The Rh sample was kept at 210 K during alkali-dosing and the SHG measurement. The sticking coefficient of alkali atoms on Rh at such a low temperature is ≈ 1 even for several adlayers. For all the three alkalis we studied (Na, K, and Cs), thermal desorption spectroscopy showed that the atoms in the second adlayer desorb at a lower temperature over a narrower range (≈ 50 K) than the atoms in the first adlayer [8]. The alkali coverage was also calibrated by the appearance of a hexagonal close-packed (hcp) LEED pattern which corresponds to a saturated monolayer. The sudden appearance of the sharp $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern at $1/3$ coverage and the sharp hcp pattern seen with further dosage indicate that the atoms in the first adlayer do not form clusters. The observed hcp LEED patterns yielded the results that the saturated monolayer coverages for Na, K, and Cs on Rh(111) are, respectively, $\theta_{\text{Na}} = 0.5$, $\theta_{\text{K}} \cong \theta_{\text{Cs}} = 0.35$ with respect to the surface density of Rh atoms ($1.6 \times 10^{15}/\text{cm}^2$). The corresponding nearest-neighbor distances for Na, K, and Cs on Rh(111) are 3.74, 4.6, and 4.6 Å, respectively, in reasonable agreement with 3.9 Å observed for Na on Ni(111) [9], 4.6 Å for K on Pt(111) [10], and 4.9 Å for Cs on polycrystalline W [11]. In this paper, we define θ' to be the fractional monolayer coverage (i.e., $\theta' = \theta/\theta_{\text{saturated monolayer}}$).

3. Results and discussion for the 1.06 μm excitation

We consider first the results in fig. 1 obtained using 1.06 μm laser excitation. As seen in this figure, the SH signal is sensitive to less than 1% of a monolayer coverage of alkali atoms. The variation of the signal with coverage is quite complicated: for $\theta' < 0.5$, the SH signals from Rh(111) with the three alkali adsorbates are nearly the same; for $0.5 < \theta' < 2.0$, they behave differently and show resonance-like peaks at $\theta' \approx 0.85$ for Na, $\theta' \approx 1$ for K, and $\theta' \approx 1.8$ for Cs; for $\theta' > 2.2$, the signals from the three alkali-covered surfaces approach different constant values.

For $\theta' < 0.3$, the SH signal increases almost exponentially with coverage. It becomes ≈ 100 times stronger than the SH signal from the bare Rh(111) metal. Such a large increase is indeed remarkable, especially since we note that the signals induced by the three different alkali adsorbates are nearly the same. One might think that the surface SHG from a metal is dominated by the free-electron contribution. Then the SH signal increase upon the adsorption of alkali atoms would then be due to the increase in the surface free-electron density resulting from the alkali atoms donating electrons to the rhodium surface. If this were the case, then the signal should be proportional to the

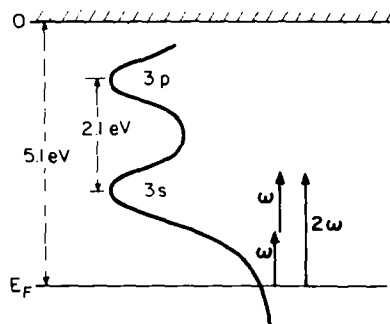


Fig. 3. A schematic energy level diagram showing the hybridized 3s and 3p bands of a Na atom chemisorbed on a metal surface positioned with respect to the Fermi level.

square of the surface free-electron density and a 100-fold increase in the signal would correspond to a 10-fold increase in the free-electron density, according to the theory of SHG from free electrons excited at frequencies far below the surface plasmon frequency [4]. This is certainly not possible considering that the fractional alkali coverage, θ' , is only 0.3. We must therefore resort to optical transitions to explain this anomalously large signal.

Let us first briefly review the theoretical understanding of the energy states of alkali atoms adsorbed on metals at low coverages [12,13]. Upon adsorption of an alkali atom on a metal surface, the energy levels of the atom hybridize with the metal electronic states and broaden into bands. The positions of the bands relative to the Fermi level are determined by the competition between the atom's desire to fill its valence shell and the electron affinity of the metal. Fig. 3 gives a sketch of the hybridized 3s and 3p bands of Na chemisorbed on a metal. The 3s band lies primarily above the Fermi level (E_F), and is therefore mostly unoccupied [12]. As a result, the adatom appears somewhat ionic with electrons partially transferred from the adatom toward the metal, creating a surface dipole. The wavefunctions of the hybridized ns states below E_F have greater amplitudes in the atom-metal bond region than those above E_F . Roughly speaking, the ns band is about 2 eV above E_F , the widths of the ns and np bands are of the order of 2 eV [12,13], and the spacing between the ns and np bands is not very different from that in the atomic case.

The above qualitative picture should also apply to other alkalis adsorbed on metal surfaces. Thus, for Na, K, and Cs on Rh(111), we simply place the ns band at ≈ 2 eV above E_F , although the actual position of the band may vary somewhat for the different alkalis [14]. The ns - np transition energies are 2.1, 1.6, and 1.4 eV for Na, K, and Cs, respectively.

In the case of a bare Rh(111) surface, the Fermi level is 5.1 eV below the vacuum level [15]. As the alkali coverage increases, interaction between the adsorbed alkali atoms becomes important. Each alkali atom experiences a

potential created by the surface dipoles on the neighboring alkali atoms [16]. This potential shifts the energy bands of the alkali together with the vacuum level downward with respect to the Fermi level, and partially immerses the ns band in the Fermi sea. By $\theta' \approx 0.5$, the Fermi level is near the center of the ns band; so the alkali atoms now appear more neutral and a further increase of the alkali coverage induces little additional level shift. The above picture is supported by the gradual decrease of the electronic work function to a minimum value as θ increases to 0.5, as well as the appearance of loss peaks in the electron energy loss spectra (EELS) [16] that may be due to transitions from the occupied ns states to the unoccupied np states.

We now discuss how the SH results in fig. 1 can be understood from the surface electronic structure described above. When an intense laser field with amplitude $E(\omega)$ at frequency ω excites the interface between 2 centrosymmetric media [characterized by dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$], the \hat{p} -polarized SH signal generated by reflection into medium 1 is given by [17]:

$$S_p(2\omega) = \alpha |k_{2,z} P_x(2\omega) + k_x (\epsilon_2(2\omega)/\epsilon'(2\omega)) P_z(2\omega)|^2, \quad (1)$$

where the constant α depends only on $\epsilon_1(2\omega)$, $\epsilon_2(2\omega)$ and the excitation geometry, $\mathbf{k}_2 = k_x \hat{x} - k_{2,z} \hat{z}$ is the SH wavevector radiated into medium 2 with \hat{z} normal to the interface, $\epsilon'(\omega)$ is the effective dielectric constant of the interfacial layer, and $\mathbf{P}(2\omega)$ is the surface nonlinear polarization. The latter is given by:

$$\mathbf{P}(2\omega) = \chi^{(2)} \mathbf{E}'(\omega) \mathbf{E}'(\omega), \quad (2)$$

where $\chi^{(2)}$ is the surface nonlinear susceptibility of the layer, and $\mathbf{E}'(\omega)$ is the effective field at ω in the interfacial layer with $E'_z(\omega) = [\epsilon_2(\omega) E_{2,z}(\omega)]/\epsilon'(\omega)$.

In our case, for $\theta' < 0.3$, the linear dielectric constants are dominated by the Rh metal and should not change drastically since the Rh plasmon frequency is ≈ 9 eV [18]. The dramatic increase in SH at low alkali coverage must come through changes in $\chi^{(2)}$.

The surface susceptibility $\chi^{(2)}$ can be calculated using second-order perturbation theory [19] and is the sum over states of terms with 3 dipole matrix elements divided by both an energy denominator at ω and one at 2ω . If we denote the hybridized ns states below E_F as $|m-ns\rangle$, and those above E_F as $\langle e-ns|$, then according to fig. 3, the dominant term in $\chi^{(2)}$ for excitation with $1.06 \mu\text{m}$ radiation should be the near-resonant terms characterized by the matrix element product:

$$\langle m-ns | \mathbf{p} | e-ns \rangle \langle e-ns | \mathbf{p} | np \rangle \langle np | \mathbf{p} | m-ns \rangle,$$

where \mathbf{p} is the dipole operator. The transitions indicated by the first and last matrix elements are near-resonant with ω and 2ω , respectively. The first matrix element $\langle m-ns | \mathbf{p} | e-ns \rangle$ refers to transitions from the occupied $|m-ns\rangle$ states and to the unoccupied $|e-ns\rangle$ states. Since it corresponds to a

bonding–anti-bonding transition, the matrix element can be large. The other two matrix elements are also large because they are connected with the strong alkali ns – np transitions. As discussed above, the original alignment of states at low alkali coverage places the center of the ns band at ≈ 2 eV above the Fermi level. The np bands are peaked at $\approx 4.1, 3.6,$ and 3.4 eV above the Fermi level for Na, K, and Cs, respectively. One sees in fig. 3 that transitions from $|m-ns\rangle$ states just below the Fermi level to $|e-ns\rangle$ and $|np\rangle$ states are still far from exact resonance with the fundamental, 1.17 eV, and the SH energy, 2.34 eV, respectively. Yet because of large matrix elements, the nonlinear susceptibility per adatom can be fairly large. As the alkali coverage increases, $\chi^{(2)}$ would increase linearly with θ' if the energy levels remain unchanged. However, the Fermi level rises with respect to the ns and np bands, bringing more ns states below the Fermi level and more $|m-ns\rangle$ – $|np\rangle$ transitions closer to 2ω resonance, and thus, enhancing the susceptibility per adatom. This qualitatively explains the sharp increase of the SH signal with θ' for $\theta' < 0.3$ in fig. 1. Between $\theta' = 0.3$ and 0.5 , the Fermi level is near the center of the ns band for all 3 alkalis. The decrease in the number of unoccupied ns states decreases the total probability of $|m-ns\rangle$ to $|e-ns\rangle$ transitions, so $\chi^{(2)}$ is expected to go through a maximum as seen in fig. 1. That the observed SHG from the three alkalis in fig. 1 are nearly the same at low coverages may also be explained by the very similar near-resonance pictures of SHG for the three alkalis discussed here.

For $\theta' > 0.5$, the almost neutral alkali adatoms are close enough to form a metallic film [18]. Over the range $0.5 < \theta' < 2.0$, the surface properties gradually change from those of a hybrid adatom–metal surface to a pure alkali metal surface. As the surface electron density increases with coverage, the plasmon frequency ω_p increases accordingly towards the final value for the pure alkali metal surface. In our SHG data of fig 1, this is evidenced by dramatic changes in signal that differ greatly for each of the alkali. Using electron energy loss spectroscopy to study alkali on Ni(100), Jostell and coworkers [16,20] found that the plasmon energy in eV is related to the fractional alkali coverage, θ' , by

$$\hbar\omega_p = \begin{cases} 3.0(\theta')^{0.4} & \text{for } 0.5 < \theta'(\text{Na}) < 2, \\ 2.3(\theta')^{0.8}, & \text{for } 0.53 < \theta'(\text{K}) < 1, \\ 1.7(\theta')^{0.8}, & \text{for } 0.69 < \theta'(\text{Rb}) < 1. \end{cases} \quad (3)$$

Presumably, ω_p for Cs on Ni(100) lies between those for K and Rb. Since the plasmon resonance is mostly a characteristic of the alkali film, we expect that the plasmon frequencies for the alkalis on Rh(111) are not very different from those on Ni(100). We then see that as θ' increases and ω_p scans through the SH frequency 2ω , $\epsilon'(2\omega)$ will go through a minimum and by eq. (1), the corresponding SH signal should exhibit a resonant feature. For Na, K, and Cs

on Rh(111), the resonance peaks are estimated from eq. (3) to be at $\theta' \approx 0.6$, 1.0, and 1.3, respectively. The experimental results in fig. 1 show the presence of the resonant peaks at $\theta' \approx 0.85$, 1.0, and 1.8 for Na, K, and Cs, respectively.

For $\theta' > 2.0$, the SH signal in fig. 1 approaches a constant value for each alkali. Actually, for $\theta' > 2.2$ measured up to $\theta' = 10$, the observed signal changes less than 5%. First, this indicates that for $\theta' > 2$, the surface has become essentially a pure alkali metal surface. That this process is incomplete by $\theta' = 1$ is reasonable since metal-adsorbate interaction should deplete some of the electron density of the alkali overlayer even at $\theta' = 1$. The electrons in the second layer are more like those of a pure alkali surface since the Rh substrate is partially screened. This conclusion is supported by the fact that the plasmon frequency also approaches its saturation value at $\theta' \approx 2$ [20]. The saturation behavior of SH shows directly that the observed SH signal must come from the topmost 1 or 2 alkali atomic layers and thus clearly demonstrates the surface specificity of the SHG technique. We point out here that with laser excitation at $1.06 \mu\text{m}$, ω and 2ω are comparable to ω_p for the alkali but are much less than ω_p for the Rh surface. It is then not so surprising that SHG from the alkali metals is 10^2 to 10^4 times larger than that from Rh because of near-resonance enhancement. The relative magnitudes of the SH signals for the alkalis are also reasonable since $2\omega < \omega_p(\text{Cs}) < \omega_p(\text{K}) < \omega_p(\text{Na})$.

4. Results and discussion for the $0.532 \mu\text{m}$ excitation

The results of SHG from alkalis on Rh(111) obtained with $0.532 \mu\text{m}$ (2.34 eV) laser radiation, shown in fig. 2, are more complicated. This is mainly because, at this laser frequency, the SH signal from Rh(111) is no longer negligible in comparison with that from the alkalis. For low coverages, interference between the Rh contribution to the SHG and that of the adsorbed alkali layer must be considered. The near-resonant transition matrix element product terms of the nonlinear susceptibility responsible for the SHG from the alkali layer, in this case, should be either

$$\langle m-ns | \mathbf{p} | e-ns \rangle \langle e-ns | \mathbf{p} | np \rangle \langle np | \mathbf{p} | m-ns \rangle$$

or

$$\langle m-ns | \mathbf{p} | np \rangle \langle np | \mathbf{p} | n' \rangle \langle n' | \mathbf{p} | m-ns \rangle$$

depending on the alkali coverage, where $|n'\rangle$ refers to states derived from alkali states higher than np . Again, the transitions indicated by the first and last elements are supposed to be nearly resonant with ω and 2ω , respectively. At very small coverages, the laser frequency ω is near the transition frequency from the occupied $|m-ns\rangle$ to the peak of the unoccupied $|e-ns\rangle$ states, as

seen in fig. 3. As the Fermi level rises relative to the ns and np bands with increasing coverage, the mean $|m-ns\rangle-|np\rangle$ transition frequency decreases toward the atomic $ns-np$ transition frequency and approaches or drops below the second harmonic frequency ($\hbar\omega = 2.34$ eV). When this happens, the real part of the nonlinear susceptibility $\chi_A^{(2)}$ due to adsorbed alkali atoms could change sign. The data for $\theta' < 0.5$ in fig. 2 can then be qualitatively understood if for very small coverages, the real parts of $\chi_A^{(2)}$ from the alkali and $\chi_{Rh}^{(2)}$ from the Rh substrate have the same sign. The SH signal should first increase with θ' , reaching a maximum around the point where the real part of $\chi_A^{(2)}$ changes sign. This explains the observed maximum around $\theta' \approx 0.15$ for K and Cs, and around $\theta' \approx 0.3$ for Na; the higher ($ns-np$) transition frequency of Na may be responsible for the large value of θ' for Na here. The signal then decrease with increase of θ' as the real part of $\chi_A^{(2)}$ partially cancels that of $\chi_{Rh}^{(2)}$, arriving at a minimum when the cancellation is complete. This could account for the observed dips at $\theta' \approx 0.3$ and 0.4 in the curves for K and Cs, respectively, in fig. 2. For Na, the same could occur at $\theta' > 0.5$ except that the adsorbed alkali atoms should form a metallic film for $\theta' > 0.5$ as we mentioned earlier. As the plasma frequency ω_p increases with coverage and approaches ω , $E'(\omega)$ in eq. (2) is resonantly enhanced as $\epsilon'(\omega)$ goes through its minimum. In the case of Na, the Sh field due to the alkali eventually cancels that from the Rh surface, leading to the dip at $\theta' \approx 0.9$. The plasmon resonance, $\omega \approx \omega_p$, is presumably responsible for the observed structure at $\theta' \approx 0.9$ for Na and K, and at $\theta' \approx 1.7$ for Cs in fig. 2. We note that the positions of these structures agree well with those of the plasmon resonance structures in fig. 1. With the $0.532 \mu\text{m}$ excitation, ω_p of the alkali films is always below 2ω . Thus, for $\theta' > 0.5$, except the resonance structures already mentioned, the SH signal should generally increase with coverage without additional resonance features due to $2\omega \approx \omega_p$. The weak bump at $\theta' \approx 1.5$ for K (not the log scale), which seems to correlate with the dip at $\theta' \approx 1.5$ for K in fig. 1, is not understood. As θ' becomes larger than 2.0, the signal from each alkali again approaches a constant value. The relative magnitudes of the SH from the three alkalis can also be explained in terms of the plasmon resonance of the films. For Cs, the SH signal is the largest as it can be enhanced by as much as $[\epsilon'(\omega)]^{-4}$ [see eqs. (1) and (2)] as ω_p is near resonance with $\theta' \approx 2$; for Na, the SH is also large because ω_p is almost in resonance [$\hbar\omega_p \approx 4.0$ eV by eq. (3)] with 2ω at $\theta' = 2$; for K, the SH is the smallest as ω_p is between ω and 2ω and is only weakly resonant with either. The relatively unimportant role of alkali in interband transitions in the SH for $0.532 \mu\text{m}$ laser excitation is supported by the lack of discernible loss peaks in EELS in the 2–5 eV range [16].

While the interpretation of the data in figs. 1 and 2 for $\theta' > 0.5$ is straightforward in terms of the plasmon resonance of the alkali film, it is less so for $\theta' < 0.5$ as it relies on our very limited knowledge about the energy bands of the alkali-derived states and their variation with alkali coverage.

However, our SH data establish the importance of dipole transitions between alkali-derived states and support the identification of the loss peaks observed in EELS with such transitions at low alkali coverage. Our interpretation of the SH data can hopefully be confirmed by studying the dispersion of SHG using a tunable laser [2] at various alkali coverages.

5. Conclusion

We have found that the alkali atoms as electron donors enhance the SHG from Rh(111) dramatically upon adsorption. The signal increase, however, does not simply arise from the increase of electron density at the surface, but is also the result of variation of optical transitions associated with the adsorbed alkali. The structure in the SH signal as a function of alkali coverage can be qualitatively understood from the shift of the Fermi level with respect to the energy bands of the alkali-derived states, and from the shift of the plasmon resonance. The adsorbed alkali form a metallic film resembling a pure alkali metal at $\theta' > 2.0$. SHG from the alkali film was found to have originated from the top surface layer ($\theta' = 2.0$) of the film. This is a clear manifestation of the surface specificity of SHG. With the $1.06 \mu\text{m}$ laser excitation, the SHG technique is so sensitive that even a 1% monolayer coverage of alkali on Rh can be readily detected.

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