CO Diffusion and Bond Weakening on Cu(410) —Probing Surface Structure—

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We discuss the possibility of using adsorbed CO for adsorbate mediated surface analysis. CO is known to exhibit properties that depend strongly on the local environment, e.g., coordination on surface sites, which manifest through its vibrational frequency. This, in turn, suggests the possibility of probing the surface structure through the changes in C−O stretching frequency during surface diffusion. Using density functional theory calculation, we demonstrate that the vibrational frequency shifts of CO manifests the corrugation of the surface, hence, its structure. To show this, we used Cu(410), a wide stepped surface, as our sample.

Keywords Density functional theory; Stepped surface; Surface diffusion

I. INTRODUCTION

Interaction of CO on metal surfaces has been extensively studied as it plays an indispensable role in industrial processes [1−8]. For example, in the Fischer-Tropsch reaction, CO reacts with H2 on metal catalysts to produce hydrocarbons. Similarly, in the water-gas-shift reaction, CO reacts with water to produce hydrogen for energy generation. Hence, investigations regarding the catalytic reactivity of surfaces are commonly benchmarked through its interaction with CO molecule. With these, experimental techniques continue to progress to understand more about molecule-surface interactions and how we can observe its manifestations [9].

Surface investigation is mostly limited to the cleanliness of the surface. Contaminants such as CO, H, and other adsorbed species interfere with spectroscopic observations for surface analysis. Recently, we proposed adsorbate mediated surface analysis where adsorbed species serve as probes for surface investigations. We have shown that adsorbed hydrogen manifest relative displacements of surface atoms through its vibrational frequency shifts [10]. In this present work, we demonstrate how we can probe surface structure using adsorbed CO. Here we will show that observable vibrational frequency shifts of CO as it diffuses on the surface reflects surface structure.

Surface diffusion of molecular species is directly influenced by the structure of the surface [11]. On flat surfaces, random walk diffusion can be observed due to the symmetry of the potential energy. On the other hand, breaking this symmetry will induce a preferable path. With the geometry of stepped surfaces, anisotropic diffusion may occur due to the asymmetric potential energy surrounding the adsorbate. Here, we use Cu(410) as the test surface structure to show such effect on an adsorbed CO molecule.

II. COMPUTATIONAL DETAILS

Experimental techniques such as scanning tunneling microscopy, helium atom scattering, and others make it possible to observe surface diffusion by obtaining snapshots of the final and initial adsorption states of a molecule [12, 13]. However, there are still limitations in visualizing the transition states between inter-site hopping. Thus, a computational approach still remains indispensable in determining the potential energy of the molecule-surface interaction during diffusion. Here, we used the density functional theory based the total energy calculation to describe the interaction of CO on Cu(410) [14, 15]. Specifically, we used Vienna ab initio Simulation Package (VASP) using projector augmented
wave (PAW) formalism and plane wave basis set, with a cutoff energy of 550 eV [16–20]. The exchange correlation was described using Perdew-Burke-Enzerhof generalized gradient (GGA) exchange correlation functional [21, 22]. We adopted the Monkhorst and Pack method to perform the Brillouin zone integrations, with $9 \times 9 \times 1$ special $k$-points [23]. Ionic relaxations were implemented with an energy convergence of less than $10^{-5}$ eV and with the Hellman-Feynman forces acting on each atom below 0.01 eV/Å. The calculated optimized bulk lattice parameter for Cu was $a_{\text{Cu}} = 3.634$ Å. To model the Cu(410) optimized structure, we used a periodic slab 16 Cu atomic layers thick [$(2 \times 1)$ surface unit cell (cf., Figure 1), with two Cu atoms per layer, topmost 8 layers allowed to relax and the last 8 layers held at their bulk-truncated positions], separated by 15 Å of vacuum along the [410] direction. To obtain the vibrational frequencies of CO, we performed finite-difference force calculation, within the harmonic approximation, as implemented in VASP.

### III. RESULTS AND DISCUSSION

#### A. Adsorption of CO on Cu(410)

In Figure 2, we plot the potential energy of an incoming CO molecule towards Cu(410) through the frozen calculation, where atoms are fixed in space at every point calculation. The total energy calculation was performed with a CO bond axis fixed along the [410] direction in a C-end configuration. The potential energy curve shows the preference of CO to bind atop the step edge atom with an adsorption energy of $-0.86$ eV. These results obtained from the constrained calculation appear to be in agreement with similar studies regarding the preferential low coordinated adsorption of CO on the Cu surface [24–26]. We also show that the binding energy of CO on Cu(410) weakens along high coordinatated adsorption sites. Hence, we see a decreasing trend in the adsorption energy from S to T3. However, fixing the CO bond axis does not take bond relaxation and reorientation into consideration. The CO molecular bond may align to a lower energy configuration after adsorption. In the case of Cu(410), CO on terrace sites may prefer to orient its bond axis along the [100] direction [27]. Thus, we implemented ionic relaxation in all the adsorption sites. Upon optimization of both surface atoms and the CO molecule, the adsorption energy is enhanced, reducing the energy difference between adsorption sites (cf., Table 1) [27]. Still, the preference of CO to bind stronger on the step edge than the terrace of Cu(410) is retained. In Figure 3, we plot the density of states (DOS) of CO/Cu(410) for three cases. For our reference, we show the molecular orbitals of CO when it is relatively far (ca. 7 Å) from the surface. We then show the DOS of the system when CO adsors atop the step edge atom, and when it is on top of the bridge site (between the step S and

![Figure 1: Top view of a $(2 \times 1)$ surface unit cell of Cu(410) with corresponding CO adsorption sites; step sites (S), terrace sites (T1, T2, T3), hollow sites (SH, T1H, T2H, T3H), and bridge sites (S–T1, T1–T2, T2–T3, T3–S) [31].](image1)

![Figure 2: Potential energy curves of CO on the top sites (bold lines), the bridge sites (thin lines), and the hollow sites (dashed lines) of Cu(410).](image2)

| Adsorption site | $E_{\text{ad}}$ (eV) (this work) | $E_{\text{ad}}$ (eV) (Kokalj et al. [27]) |
|----------------|-------------------------------|----------------------------------|
| S              | $-0.92$                       | $-0.89$                          |
| T1             | $-0.87$                       | $-0.84$                          |
| T2             | $-0.83$                       | $-0.82$                          |
| T3             | $-0.88$                       | $-0.84$                          |
| T1–T2          | $-0.77$                       | $-0.78$                          |
| T2–T3          | $-0.84$                       | $-0.84$                          |
| T3–S           | $-0.91$                       | $-0.88$                          |
| T1H            | $-0.82$                       | $-0.84$                          |
| T2H            | $-0.77$                       | $-0.82$                          |
| T3H            |                                |                                  |
the nearest terrace atom T1). Here, we see the known interaction of CO with metal surfaces. For both configurations there is a donation of the $\sigma$ electrons from CO to Cu and a back-donation of the d electrons to the lowest unoccupied molecular orbital (LUMO) of CO. This $\pi^*$ antibonding state of CO is partially filled upon adsorption and in turn weakens its molecular bond. This becomes more pronounced when CO adsorbs on the bridge site of the surface. This results in a more elongated CO bond on the bridge site S–T1 than on the step site S.

**B. Diffusion of CO on Cu(410)**

In Figure 4, we show the two-dimensional (2D) potential energy surface (PES) of CO on Cu(410) with coordinates along the [410] direction and diffusion coordinates (0–12) and (0–6) along the (100) terrace and the step edge, respectively. These diffusion coordinates locate on top, bridge and mid(top-bridge) sites of Cu(410). A step increment of 0.2 Å along the diffusion coordinate was implemented for a fine energy resolution of the potential energy surface. The Cu–Cu distances between the adjacent surface atoms along the terrace and the step edge are 2.6 and 3.6 Å, respectively. Hence, the step size allows at least 11 diffusion points between the top sites, with midpoints lying on the bridge sites. Tracing the least energy path for diffusion, we optimized the CO bond length and orientation, with C fixed along the diffusion points. From the potential energy curve of partially constrained CO, we can estimate the diffusion barriers between consecutive top sites. Here, we observe anisotropic potential energy barriers due to differently coordinated surface atoms. In Figure 4a (right panel), the potential energy curve manifests irregular peaks in-between the top sites upon partially constrained relaxation. These arise due to the geometry of the surface, resulting in an asymmetric interaction of CO between two top sites of different coordination.
In addition, the relative stability of CO at points near the bridge sites contributes to the “spiky” profile along the diffusion path. Nevertheless, in general, we can see a down slope trend of the potential energy from the valley site towards the step edge site. The climbing nudge elastic band (cNEB) was then implemented to obtain a more accurate estimate of the energy barriers [28]. The barriers obtained from the partially constrained PES and cNEB shows a similar trend between diffusion paths, with an energy difference of 0.02 to 0.05 eV (cf., Figure 5). From here, we obtained the hopping rates for each diffusion paths [29, 30]. In Figures 5 and 6, we represent the inter-site hopping configurations to be (initial site $$\rightarrow$$ final site). So, (T3$$\rightarrow$$T2, T2$$\rightarrow$$T1, T1$$\rightarrow$$S) refers to diffusion towards the step edge and the reverse (S$$\rightarrow$$T1, T1$$\rightarrow$$T2, T2$$\rightarrow$$T3) refers to diffusion away from the step edge. S$$\rightarrow$$S refers to diffusion between the step atoms. The initial- and final-state configurations were taken from fully optimized structures of CO/Cu(410) atop the surface atoms. The hopping rates at lower temperatures imply that a CO molecule on the Cu(410) surface has a higher chance of diffusing towards the step edge than in the opposite direction. It can also be noted that a step to terrace hopping is more likely to occur than an inter-step hopping. As well, we can see that the CO molecule tends to stay along the first 3 atomic layers (S, T1, T2) of Cu(410). Hence, we can observe an anisotropic diffusion of the CO molecule on Cu(410) which may not be possible on a flat surface. On a side note, this partly explains the known reactivity of the stepped surfaces where it induces surface diffusion towards the reactive step edge site.

C. Vibrational frequency of CO on Cu(410)

So far, we have shown the effect of the surface structure of Cu(410) on the mobility of CO and how the CO bond is perturbed by site coordination. Now, we demonstrate how CO weakens its molecular bond as it diffuses on the Cu(410) surface. In Figure 7, we show the changes in the bond length of CO with corresponding shifts in its vibrational frequency. In an experiment on CO adsorption on Cu(410), infrared reflection-absorption spectroscopy (IRAS) results show the existence of a high frequency peak of 2099 cm$$^{-1}$$ and an emergence of a lower broadened peak of about 2048 cm$$^{-1}$$ at high coverages [26]. These peaks correspond to CO atop the step edge atom and the terrace atoms, respectively. With the previously mentioned diffusion coordinates, we calculated the C$$\rightarrow$$O stretching frequency within the harmonic approximation. Starting atop step atom at 2032 cm$$^{-1}$$, the vibrational frequency of C$$\rightarrow$$O stretching on top of the surface atoms (S, T1, T2, T3) exhibits a decreasing trend towards the valley. The CO molecules on T1 and T2 have lower vibrational frequencies (with shifts of around 33$$-$$37 cm$$^{-1}$$) with respect

![Figure 5: Energy barriers for CO diffusion along the diffusion paths between step (S) and terrace (T) atoms of Cu(410), obtained from cNEB (red) and PES of partially constrained CO (black).](image)

![Figure 6: Approximate temperature dependent hopping rates of CO for translations toward (solid lines) and away from (dashed lines) the step edge.](image)

![Figure 7: Wavenumber (orange) of C$$\rightarrow$$O stretching and its corresponding bond length (blue) for diffusion along a) the (100) terrace and b) the step edge.](image)
to that on S. This is slightly lower than the experimental frequency difference of 51 cm$^{-1}$ between CO atop S and terrace atoms. Nevertheless, the decreasing trend from the step to the terrace agrees well with the experiment [26]. This trend can also be seen along the bridge sites (S–T1, T1–T2, T2–T3). Interestingly, an alternating vibrational shift occurs in between the consecutive surface atoms. A decrease in vibrational frequency from S to S–T1 and an increase from S–T1 to T1. Note, however, that the increase from S–T1 to T1 is less than the drop from S to S–T1. This is due to the lower coordination of S as compared to T1. A comparable decrease and increase in the frequency between T1 and T2 can also be observed due to nearly the same coordination. This trend continues to T3. In the same way, the step-to-step decrease and increase in the vibrational frequency between T1 and T2 simply reflects the surface corrugation of the stepped surface. These shifts in the vibrational frequency simply reflects the surface structure of Cu(410) probed by a moving CO adsorbate.

**IV. CONCLUSION**

As a common surface contaminant, a CO adsorbate can be potentially used as a surface probe through monitoring its vibrational shifts during surface diffusion. Here, we show that the vibrational frequency shifts of CO corresponds to the atomic corrugation of the Cu(410) surface and manifests its stepped structure. With the resolution of current spectroscopic techniques, these shifts can be observable. Thus, with this simple demonstration, we propose the possibility of using adsorbed CO for adsorbate mediated surface analysis towards the fine structural investigation.

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