

# Site-Hopping of Adsorbed CO in $c(4\times 2)$ -CO/Ni(111) by Laser-Induced Temperature Jump: Time-Resolved Sum-Frequency Generation Observation

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The  $c(4\times 2)$ -CO/Ni(111) surface under pulsed near-infrared irradiation is examined by time-resolved sum-frequency generation (SFG) spectroscopy. At a surface coverage of 0.5, the surface is confirmed to consist almost exclusively of hollow CO molecules, as evidenced by a sole SFG peak at  $1904\text{ cm}^{-1}$ . Under pulsed irradiation, this peak weakened, followed by the emergence of a new peak attributable to atop CO. This represents a direct observation of site-hopping of adsorbed CO. The hopping phenomenon was found to be entirely transient, with the surface returning to the pre-excited state within a few hundred picoseconds without desorption. The dynamics of the process are also discussed.

## 1. Introduction

Adsorbed CO on metal surfaces, one of the simplest adsorbates, has attracted significant interest in the study of catalysis, and the temporal behaviors of these adsorbates have been investigated extensively by ultrashort laser spectroscopy.<sup>1–8</sup> The desorption of CO under pulsed laser irradiation has been monitored by mass analysis<sup>4,5</sup> or surface spectroscopy,<sup>6</sup> and the spectral change of thermally or vibrationally excited CO on surfaces has been examined by surface vibrational spectroscopy.<sup>7,8</sup> Only a few attempts have been made, however, to make direct observations of chemical reactions at surfaces initiated by pulsed laser pumping.<sup>9,10</sup> Site-hopping of adsorbates among adsorption sites is also a topic of interest, and is expected to play an important role in surface phenomena such as diffusion of adsorbed species, island formation and adsorption-assisted desorption.<sup>11</sup>

Irradiation with near-infrared (NIR) pulses thermally excites the surface, giving rise to a change in surface vibrational spectra.<sup>4–10</sup> The CO stretching mode of adsorbed CO is unharmonically coupled with low-frequency frustrated modes, and thermal excitation causes a frequency shift and broadening of the CO stretching mode.<sup>7,8,12–14</sup> Irradiation with intense pulses also results in desorption of CO from the surface,<sup>4,5</sup> with kinetics well explained by the rate equation of a thermal process.

Infrared-visible sum-frequency generation (SFG) is a nonlinear wave mixing, and when coupled with IR active vibrational resonances, is an effective tool for surface spectroscopy. Time-resolved spectroscopy can be performed by employing ultrashort pump and probe pulses. This technique has been successfully applied to the study of surface dynamics.<sup>1–3</sup>

The adsorption of CO on Ni(111) has been investigated extensively.<sup>15–27</sup> At a CO/Ni ratio of  $\theta = 0.5$ , a  $c(4\times 2)$  CO structure is formed, and in the IR spectrum, only the resonance

corresponding to the vibrational frequency of the bridged (2-fold hollow) CO molecule is observed.<sup>17,20–23</sup> This is in contrast to the assignments by X-ray diffraction, which would indicate that the structures are 3-fold hollow.<sup>26,27</sup> In this paper, CO in the  $c(4\times 2)$  structure is referred to as hollow CO for simplicity. At lower ratios of coverage, the IR peak of 3-fold hollow CO, at a resonance frequency different from that of the bridged CO, can be clearly observed.<sup>23</sup> At the saturation coverage of  $\theta = 0.57$ , the layer consists of 25% atop CO.<sup>16,18,20</sup>

The difference between the potentials of hollow CO and atop CO on Ni surfaces is not great, and site-hopping between these sites has often been observed by surface spectroscopy.<sup>30–32</sup> These previous studies focused on the migration of quenched CO molecules to stable sites. The aim of the present study is to demonstrate CO site-hopping to upper unstable sites from stable hollow sites by pulsed laser irradiation. Time-resolved SFG is performed using NIR (1064 nm) pump pulses to induce the temperature jump. Without laser pumping, the hollow CO of the  $c(4\times 2)$  layer on Ni(111) does not exhibit site-hopping to different sites even when the surface temperature is raised by conventional heating. When pumped by NIR pulses, however, the population of hollow CO is observed to decrease with a corresponding increase in atop CO.

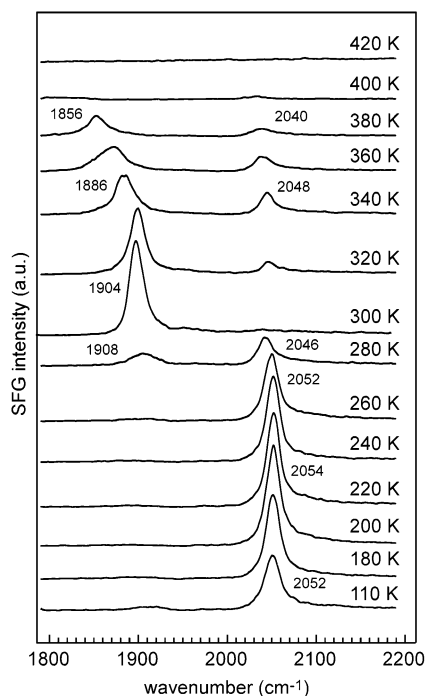
## 2. Experimental Section

SFG spectra were obtained using frequency-tunable IR and 532 nm visible pulses generated by a mode-locked Nd:YAG laser (pulse width of 35 ps and repetition rate of 10 Hz).<sup>9,10,27,28</sup> The second harmonics pulse at 532 nm was converted to a frequency-tunable NIR pulse by parametric generation/amplification using two  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystals. The frequency-tunable IR (1300–3000  $\text{cm}^{-1}$ ) pulse was generated by difference frequency generation using an AgGaS<sub>2</sub> crystal from the tunable NIR line and the fundamental output of the Nd:YAG laser at 1064 nm. The energy of the probe IR and visible pulses at the sample surface were 50  $\mu\text{J}/\text{pulse}$  (at 2000  $\text{cm}^{-1}$ ) and 100  $\mu\text{J}/\text{pulse}$ , respectively, and both were p-polarized at the sample surface. The fundamental (1064 nm) pump pulse of 10 mJ/pulse

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**Figure 1.** SFG spectra of CO/Ni(111) as a function of annealing temperature. CO was adsorbed at saturation coverage at 110 K, and the surface was instantaneously annealed at the stated temperatures. All spectra were recorded at 110 K.

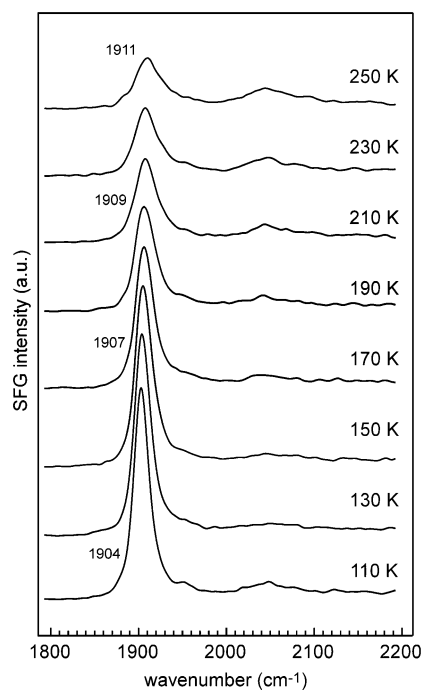
was passed through a variable optical delay to irradiate the sample surface. The beam diameters of the IR, visible, and pump NIR pulses were approximately 2, 3, and 4 mm, respectively. The SFG signal was detected by a photomultiplier tube after passing through optical filters and a monochromator.

The Ni(111) sample was handled in an ultrahigh vacuum chamber with a base pressure of  $2 \times 10^{-8}$  Pa. The surface was cleaned by repeated  $\text{Ar}^+$  bombardment and annealing at 1000 K. CO gas was introduced into the chamber by a variable leak valve.

### 3. Results and Discussion

**3.1. SFG Spectra without Pumping.** The Ni(111) surface was covered with CO at saturation coverage at 110 K, and the surface was annealed for several seconds at various temperatures. Spectral measurements were performed at 110 K after annealing. Figure 1 shows the SFG spectra for annealing temperatures up to 420 K. In the range 110–260 K, a peak corresponding to atop CO was observed at  $\sim 2050 \text{ cm}^{-1}$ . In this temperature range, the Ni(111) surface was saturated with CO at a coverage of  $\theta = 0.57$ ,<sup>16,18,20</sup> and the adsorption layer consisted of 75% hollow CO and 25% atop CO. Although the peaks assigned to hollow CO and atop CO are observable in infrared reflection absorption spectra (IRAS)<sup>20–23,25</sup> and high-resolution electron energy loss spectra (HREELS),<sup>17,24</sup> the peak attributable to hollow CO is suppressed in SFG spectra at the present coverage, as reported previously.<sup>28,29</sup>

Adsorbed CO began to desorb above an annealing temperature of 280 K, and a SFG peak of hollow CO appeared at  $1908 \text{ cm}^{-1}$ . Weakening of the signal of atop CO and appearance of the peak of hollow CO occurred simultaneously. Surfaces annealed at 300 K have been shown to form the ordered  $c(4 \times 2)$  structure with coverage of  $\theta = 0.5$  and no occupied atop sites.<sup>20,22</sup> This was reconfirmed in the present observations, as only the signal attributable to hollow CO was observed. The surfaces at higher annealing temperature exhibited both hollow



**Figure 2.** SFG spectra of CO/Ni(111) at  $\theta = 0.5$  as a function of substrate temperature. The CO-saturated surface was annealed at 300 K to obtain coverage of 0.5, and the spectra were recorded at the stated temperatures.

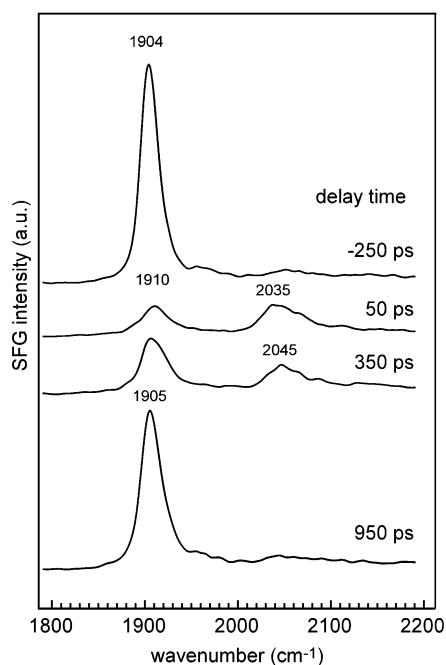
and atop CO peaks, reflecting the disruption of the  $c(4 \times 2)$  structure. The CO molecules fully desorbed at 420 K.<sup>21</sup> These behaviors are in qualitative agreement with previous studies,<sup>15–27</sup> except for the intensity screening of the hollow CO peak by the presence of the atop CO at saturation coverage.<sup>28,29</sup>

The CO/Ni(111) surface at a coverage of  $\theta = 0.5$  is examined in more detail in Figure 2. This system was prepared by annealing a saturated CO/Ni(111) sample at 300 K. After annealing, the substrate temperature was set as indicated in the figure for spectral measurements. A peak due to hollow CO at  $\sim 1904 \text{ cm}^{-1}$  is predominant at substrate temperatures of between 110 and 250 K. At 250 K a weak and broadened feature around  $2040 \text{ cm}^{-1}$  becomes noticeable, due to a small amount of atop CO possibly originating from experimental error in the estimated coverage of  $\theta = 0.5$  ( $c(4 \times 2)$ ). This signal of atop CO is much smaller than that observed in the pump–probe experiments, as described later. The CO layer at  $\theta = 0.5$  therefore consisted primarily of hollow CO, which was largely immobile even when the substrate temperature was increased in this temperature range.

The stable  $c(4 \times 2)$  structure at up to 300 K has been well established in previous work,<sup>12–14,20,22</sup> and the thermal broadening and shift have been interpreted by theory.<sup>12–14</sup> In general, the populations of hollow CO and atop CO are in equilibrium determined by the temperature and coverage ratio. However, this is not the case for  $\theta = 0.5$ .<sup>22</sup> The line width of the hollow CO peak broadens and weakens with increasing temperature. Thermal excitation of the frustrated motions of hollow CO is the key factor for this spectral change.<sup>12–14</sup>

The present observations of the static spectral feature as a function of coverage and temperature are consistent with previous reports.<sup>13,14,20–23</sup>

**3.2. Time-Resolved SFG Spectra under NIR Pumping.** The surface was again prepared by annealing a saturated CO/Ni(111) sample at 300 K. The time-resolved measurements were then carried out at 120 K. The transient SFG spectra at various



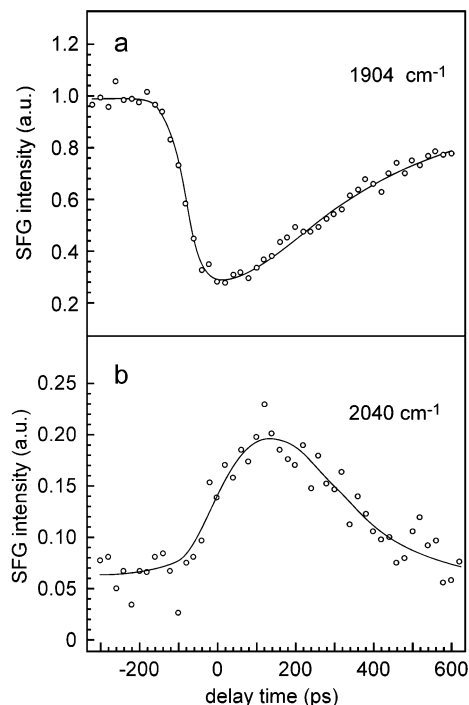
**Figure 3.** Transient SFG spectra of CO/Ni(111) for  $\theta = 0.5$  at 120 K.

delay times after pumping are shown in Figure 3. At  $-250$  ps (i.e., before irradiation), only hollow CO was observed ( $1904\text{ cm}^{-1}$ ), and the SFG spectrum was identical to that in Figure 2 at the given temperature. The surface returned to the same state after each pump–probe cycle of 100 ms. This experiment was carried out in a vacuum, so that irradiation-induced desorption did not take place.

When the surface was irradiated by the NIR pulses, the temperature jumped and reached a maximum at 50 ps. The time profile was predicted by solving a heat-diffusion equation.<sup>9,10</sup> In the spectrum at 50 ps, the peak due to hollow CO was significantly weakened and a new peak appeared at  $2035\text{ cm}^{-1}$ . This new peak is assigned to atop CO by comparison with the corresponding spectra at higher temperatures in Figure 1. The population of hollow CO therefore decreased upon irradiation and rapid heating, with a corresponding appearance of atop CO.

The magnitude of this temperature rise was estimated to be  $\sim 300\text{ K}$ , indicating a surface temperature of up to  $\sim 430\text{ K}$  at 50 ps,<sup>9,10</sup> which is much higher than the desorption temperature. Although hollow CO at  $\theta = 0.5$  is stable at a substrate temperature of below  $260\text{ K}$  (see Figure 1), it is induced to site-hop when it is heated rapidly by the short pump pulse to above the desorption temperature. This site-hopping would occur from hollow CO to atop site as well as various other surface sites, and the adsorbed CO may have in fact been widely distributed during and immediately following the NIR excitation.

The obvious weakening in the SFG signal of hollow CO has been ascribed to the thermal excitation of low-frequency modes of the hollow CO,<sup>7,8,12–14</sup> as well as to a decrease in the population of hollow CO due to site-hopping. At present, quantitative analysis to separate the two contributions is difficult. Qualitatively, the number of hopping CO molecules can be considered very small on the basis of the following argument. The frequency of hollow CO at  $1904\text{ cm}^{-1}$  blue-shifts to  $1910\text{ cm}^{-1}$  by pumping. If the number of hollow CO decreased dramatically, the resonance frequency should in fact red-shift because of dipole–dipole interaction.<sup>33</sup> Thus, the observed blue-shift is attributable mainly to thermal excitation of the frustrated modes coupled to the vibrational mode of nonhopping hollow CO.<sup>13,14</sup>



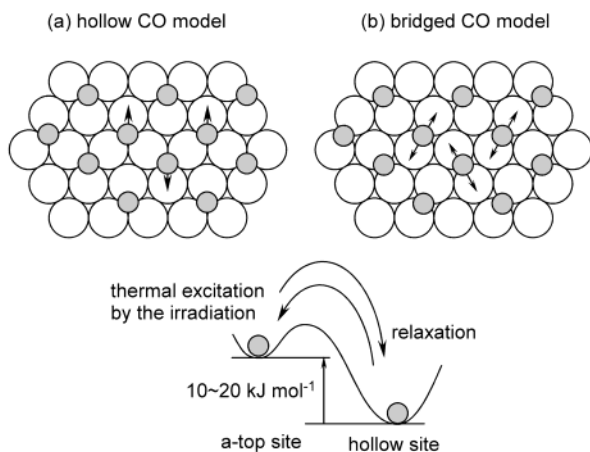
**Figure 4.** Transient changes in SFG signals at (a)  $1904\text{ cm}^{-1}$  for hollow CO, and (b) at  $2040\text{ cm}^{-1}$  for atop CO at 120 K.

At 350 ps, the intensity ratio of the hollow CO and atop CO peaks had returned, but were still lower than before pumping. At 950 ps, the spectrum had almost recovered to the prepumping state. The peak due to hollow CO was still slightly broadened and weakened at this time, indicating that the surface was still hotter than the initial temperature. Although longer delays could not be scanned due to the limitations of the optical delay circuit used, the spectrum had recovered by the next measurement of the next irradiation pulse. This indicates that the observed site-hopping is a transient phenomena and is not a process leading to desorption or one-way migration. The four spectra in Figure 3 were obtained by accumulated measurement of 32 000 pulses, confirming this hopping phenomenon to be entirely transient and cyclic.

The signal intensities at  $1904$  and  $2040\text{ cm}^{-1}$  are recorded against delay time as shown in Figure 4. The intensity at  $1904\text{ cm}^{-1}$ , due to hollow CO, first decreases upon irradiation, whereas the intensity of the  $2040\text{ cm}^{-1}$  peak of the atop CO increases. Note the slight delay between the immediate drop in the hollow CO signal and the subsequent strengthening of the atop CO signal. To interpret this time profile, two different effects have to be taken into account; the change in the population itself, and the thermal broadening/weakening of the atop CO peak.<sup>7,8</sup> The recovery profiles of both the hollow and atop signals reflect that variation in surface temperature according to heat diffusion on a metal surface.<sup>4–10</sup> A quantitative analysis of this mechanism will be given elsewhere.

**3.3. Remarks.** There are two possibilities for the location of CO molecules in the  $c(4\times 2)$  structure at  $\theta = 0.5$ ; the 3-fold hollow site and the bridged (2-fold hollow) site (Figure 5). Although treated simply as hollow CO for simplicity of the discussion above, the two forms are distinguished here. A small fraction of the CO molecules move to the neighboring atop sites over a period of a few hundred picoseconds after the NIR pump pulse. For the molecules to be able to move, the accepting Ni atom should not be bonded to other CO molecules. The two cases differ on this point: for 2-fold hollow CO, two of the adjacent atop sites are unbound, whereas only one free atop





**Figure 5.** Model of site-hopping of CO for (a) 3-fold hollow CO, and (b) bridged CO, with potential diagram.

site is available for the 3-fold hollow CO. It is reasonable to assume the hopping probability is affected by the number of accepting sites as well as by the potential profile, as depicted in the bottom scheme of Figure 5.

Site-hopping of adsorbates has been studied at cryogenic temperatures, at which surface molecules adsorbed at low-temperature begin to migrate upon heating.<sup>30–32</sup> In this case, the molecules are first adsorbed at various quasi-stable states and then move to more stable sites when the temperature rises. The present observations do not follow this model. The stable surface molecules are rapidly heated to above the desorption temperature by pulse irradiation, causing the surface molecules to excite into unstable sites for a short period. This kind of transient behavior of adsorbed molecules has also been observed on the formate/NiO(111) system, where the same spectroscopic technique was employed to find the conversion of stable bidentate formate to the unstable monodentate formate.<sup>9,10</sup>

Quantitative analysis is required to obtain detailed information on the potential profiles for site-hopping. To achieve such analysis, the SFG signal intensity is currently being calibrated as a measure of the population of hollow/atop CO molecules. There are many factors to be taken into account in such work, including the nonlinear nature of the SFG as a second-order effect,<sup>1–3</sup> nonlinearity due to dipole–dipole coupling between the adsorbed CO molecules,<sup>33</sup> the screening effect when hollow and atop CO molecules coexist,<sup>28,29</sup> and the intensity change due to thermal agitation of the low-frequency modes coupled to the CO stretching mode.<sup>7,8</sup>

A qualitative picture of the potential difference can be derived by taking the stability of the  $c(4 \times 2)$  structure when heated conventionally (260 K) and the appearance of the atop CO by temperature jump to higher than the desorption temperature ( $\sim 430$  K). On the basis of simple equilibrium, the ratio of populations can be derived as  $\theta_{\text{a-top}}/\theta_{\text{hollow}} = \exp(-\Delta E/RT)$ , where  $\theta$  is the partial coverage,  $\Delta E$  is the energy difference,  $R$  is the gas constant, and  $T$  is temperature. The potential difference between hollow and atop CO is then roughly approximated to be  $10\text{--}20 \text{ kJ mol}^{-1}$ . However, as the time profile in this study follows the temperature profile of a heated metal surface, the rate of reaction could not be determined. A more accurate analysis through detailed pump–probe experiments over chang-

ing substrate temperature and pulse energy will be published in a forthcoming paper.

#### 4. Conclusion

A pump–probe technique was successfully applied to observe the site-hopping of CO molecules on Ni(111) at a surface coverage of  $\theta = 0.5$ . At this coverage and in the steady state, this system consisted solely of hollow CO, as evidenced from the single SFG peak at  $1904 \text{ cm}^{-1}$ . Upon NIR pulsed irradiation, the population of hollow CO dropped immediately, followed momentarily by an increase in atop CO due to the temperature jump at the surface. The hollow CO was found to migrate to neighboring atop sites, which are at higher energy than the hollow site. This unstable CO returned to the lower energy hollow site as the substrate temperature again returned to ambient conditions.

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