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## Photoinduced Surface Dynamics of CO Adsorbed on a Platinum Electrode

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The surface dynamics of adsorbed CO molecules formed by dissociative adsorption of HCHO at a polycrystalline Pt electrode/electrolyte solution interface was studied by picosecond time-resolved sum-frequency generation (TR-SFG) spectroscopy. A SFG peak at 2050–2060  $\text{cm}^{-1}$  was observed at the Pt electrode in  $\text{HClO}_4$  solution containing HCHO at 0–300 mV (vs Ag/AgCl), indicating the formation of adsorbed CO at an atop site of the Pt surface as a result of dissociative adsorption of HCHO. The peak position varied with potential by  $\sim 33 \text{ cm}^{-1}/\text{V}$ , as previously found in an infrared reflection absorption spectroscopy (IRAS) study. Irradiation of an intense picosecond visible pulse (25 ps, 532 nm) caused an instant intensity decrease and broadening of the CO peak accompanied by the emergence of a new broad peak at  $\sim 1980 \text{ cm}^{-1}$  within the time resolution of the system. These results suggest a decrease and increase in the populations of CO adsorbed on atop and bridge sites, respectively, upon visible pump pulse irradiation.

### Introduction

The dynamics of interactions between molecules and a surface such as vibrational excitations, energy exchange, and relaxation is of fundamental importance in surface science.<sup>1,2</sup> The time scale of these processes is in the pico- to femtosecond regime. Recent development of short pulse laser techniques has enabled direct observation of ultrafast surface dynamics. These techniques make it possible not only to identify the surface species but also to probe the transient species generated by the pump pulse in real time.<sup>3–5</sup> Sum-frequency generation (SFG) spectroscopy is becoming a major tool in surface science because of its high surface/interface selectivity and versatile applicability.<sup>6–8</sup> Although most of the SFG studies so far have been concerned with the static structure of molecules at interfaces, a more important contribution of SFG spectroscopy should be its high time resolution, and time-resolved sum-frequency generation (TR-SFG) spectroscopy is expected to become one of the most powerful methods for observing and identifying transient states of surface adsorbates.<sup>9–16</sup> Although most of the TR-SFG studies have been carried out in an ultrahigh vacuum (UHV) environment, TR-SFG is more important for study at solid/liquid interfaces, which can be probed only by limited techniques.

Adsorbed CO on a metal surface is one of the simplest adsorbates and has attracted significant interest in the study of fundamental surface science, catalysis, and electrochemistry. An understanding of the oxidation mechanism of adsorbed CO is important to design and develop electrocatalysts for fuel cells,<sup>17–21</sup> and the surface dynamics of adsorbed CO on an

electrode surface in an electrolyte solution should therefore be investigated.

TR-SFG seems to be an ideal tool to study the surface dynamics of adsorbed CO at a solid/liquid interface. Although there are several reports of TR-SFG study on an electrode, those reports are only of investigations of vibrational relaxation lifetime by IR excitation.<sup>14–16</sup>

In the present study, we investigated the SFG response of CO adsorbed on a Pt electrode surface in an electrolyte solution to irradiation of intense visible pulses as in the time resolution of  $\sim 20$  ps. Upon visible pulse irradiation, the population of on-top CO instantly decreased accompanied by an increase in multibonded CO due to the transient temperature jump at the surface. It recovered to the initial value within 100 ps. This is the first study showing a transient reversible migration of CO molecules adsorbed on a Pt surface under electrochemical conditions in a picosecond time domain.

### Experimental Section

The SFG system used in the present study was described in detail elsewhere.<sup>23</sup> Briefly, a picosecond Nd:YAG laser (EK-SPLA, PL2143B) with a 25-ps pulse width and repetition rate of 10 Hz was employed to pump an OPG/OPA/DFG (EKSPLA, PG401VIR/DFG) system, which generates tunable infrared pulses. The loosely focused visible (70  $\mu\text{J}/\text{pulse}$  energy) and IR (200  $\mu\text{J}/\text{pulse}@5000 \text{ nm}$ ) beams were overlapped at the sample surface. The incident angles of the visible and IR beams were about 70 and 50°, respectively. The second harmonic output (532 nm) from the Nd:YAG laser was divided into two beams to be used for the pump pulse of pump–probe SFG measurements and a frequency fixed pulse to generate SF light at the sample surface. The SF signal was separated from the reflected visible and IR pulses by passing through irises and a

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monochromator (CHROMEX, 501I) and was detected by a photomultiplier tube (Hamamatsu, R3896) and normalized to the intensities of the IR and visible pulses. Temporal and spatial overlaps were adjusted by monitoring the SFG signal from a quartz plate. The polarization combination was (ppp), where the first, second, and third letters in parentheses denote the polarization of SF, visible beams, and IR beams, respectively, and p polarized light was used for the pump pulse (fluence 1.4 mJ/cm<sup>2</sup>). SFG measurements were carried out at room temperature (~22 °C).

Electrochemical measurements were carried out using a spectroelectrochemical cell made of Kel-F. A Ag/AgCl (saturated NaCl) and a Pt wire were employed as a reference electrode and a counter electrode, respectively. The working electrode was a polycrystalline Pt disk of 10 mm in diameter held in a Kel-F holder. The electrolyte solutions (0.1 M HClO<sub>4</sub>, 0.1 M HCHO) were prepared using reagent grade HClO<sub>4</sub> (Wako Pure Chemicals) and HCHO (Wako Pure Chemicals) and purified water provided by a Milli-Q system (Millipore Inc.) and deaerated by bubbling high-purity Ar gas (99.999%) prior to the spectroelectrochemical measurements. The electrode potential was controlled with a potentiostat (Toho Technical Research, PS-07). The electrode potential, current, and SFG signal were recorded by using a personal computer (Compaq, DeskPRO 2000) through a 13-bit AD converter (Stanford Research System, SR245).

After introduction of the working electrode to the spectroelectrochemical cell, electrochemical cleaning cycles, which consisted of continuous potential cycling between -0.25 and 1.15 V in 0.1 M HClO<sub>4</sub> solution, were performed before each electrochemical SFG experiment until the cyclic voltammogram (CV) became that of a clean Pt electrode. Then, the electrolyte solution was changed to HCHO-containing solution while keeping the electrode potential at 0 mV. The Pt electrode was then gently pushed against the CaF<sub>2</sub> window of the spectroelectrochemical cell to achieve a thin layer (~5 μm) configuration, thus avoiding strong absorption of the IR beam by the electrolyte solution.

The SFG spectra were analyzed by using the following equation:<sup>24</sup>

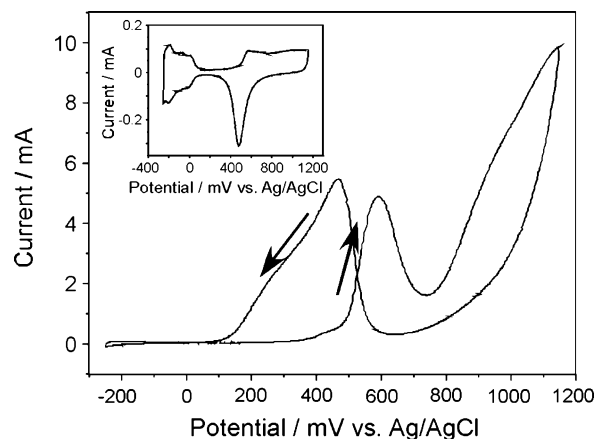
$$I_{\text{SFG}} = \left| \chi_{\text{NR}}^{(2)} + \frac{A_0 e^{i\varphi}}{\omega - \omega_0 + i\Gamma_0} \right|^2 \quad (1)$$

where  $\omega$  is the infrared frequency,  $\chi_{\text{NR}}^{(2)}$  is the nonresonant contribution to the surface nonlinear susceptibility, and  $\omega_0$ ,  $A_0$ ,  $\varphi$ , and  $\Gamma_0$  are the resonant frequency, transition amplitude, phase difference between resonant and nonresonant terms, and homogeneous width, respectively.

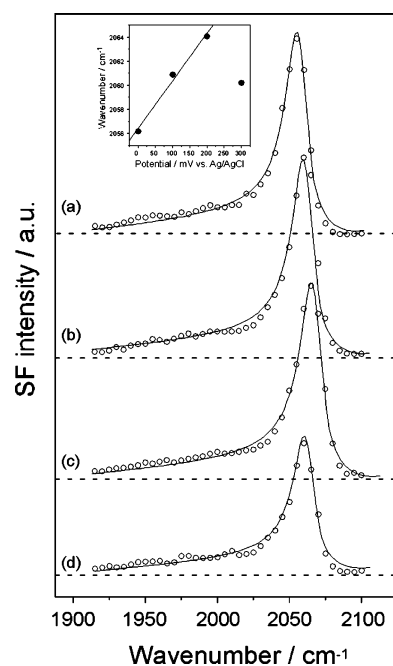
## Results and Discussion

Figure 1 shows CVs of the Pt electrode in 0.1 M HClO<sub>4</sub> solution with and without (inset) 0.1 M HCHO. They are in good agreement with the results reported before.<sup>22</sup> The hydrogen waves in the potential range between -250 and ~50 mV (inset) were suppressed in the solution containing HCHO, indicating the existence of a CO adlayer on the Pt electrode surface.<sup>20,21</sup>

SFG measurements were carried out in the potential range between 0 and 300 mV, in which the presence of adsorbed CO was expected, after a CO adlayer was established at 0 V. Figure 2 shows SFG spectra of the Pt electrode in 0.1 M HClO<sub>4</sub> solution containing 0.1 M HCHO at various potentials. A strong peak centered at ~2055 cm<sup>-1</sup> was observed, in agreement with results of a previous study by infrared spectroscopy,<sup>25</sup> and was assigned

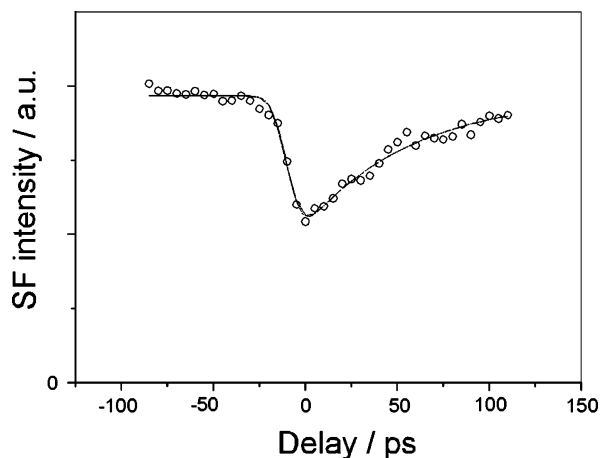


**Figure 1.** Cyclic voltammogram of the Pt-poly electrode in 0.1 M HClO<sub>4</sub> + 0.1 M HCHO with a sweep rate of 20 mV/s. Inset: cyclic voltammogram of the Pt-poly electrode in 0.1 M HClO<sub>4</sub> with a sweep rate of 20 mV/s.

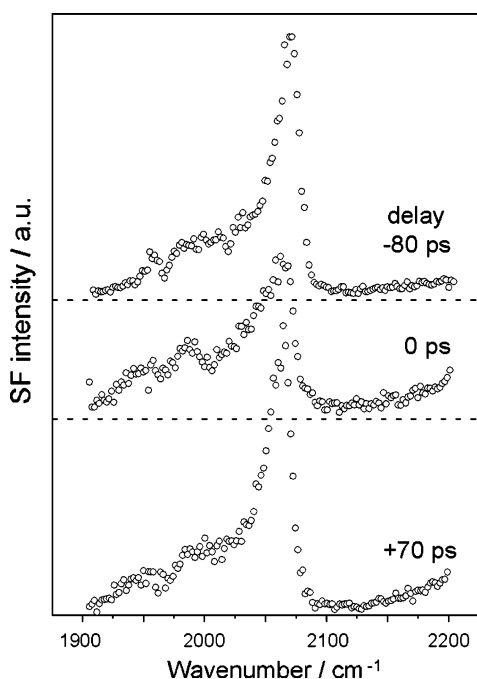


**Figure 2.** SFG spectra of the Pt surface in a solution of 0.1 M HCHO in 0.1 M HClO<sub>4</sub> as a function of the applied potential: (a) 0 mV; (b) 100 mV; (c) 200 mV; (d) 300 mV.

to the stretching vibration of CO ( $\nu_{\text{CO}}$ ) adsorbed at a 1-fold coordinated (atop) site of the Pt surface. As the potential was changed positively, the peak position of this band shifted to a higher wavenumber by approximately 33 cm<sup>-1</sup>/V up to 200 mV (Figure 2 inset), which also agrees with the previous results of IR spectroscopy.<sup>25</sup> This shift has often been referred to as electrochemical Stark tuning. Intensity decrease and red shift of SFG spectra were observed at 300 mV, indicating the loss of CO coverage resulting from CO oxidation. When the potential was made more positive, an SFG peak was not observed (data not shown), indicating complete loss of CO from the Pt surface. The CO oxidation threshold potential observed by SFG in our experiments was ~200 mV more negative than that expected from the CV (Figure 1). A discrepancy between the CO oxidation potential measured by voltammetry and the potential of the disappearance of the SFG signal was previously reported,<sup>26,27</sup> and it is thought to be due to the different data acquisition times, since measurements of each SFG spectrum



**Figure 3.** Temporal profile of the SFG signal intensity at  $2055\text{ cm}^{-1}$  at a potential of 0 mV. The solid line is the result of a least-squares fitting (see text).

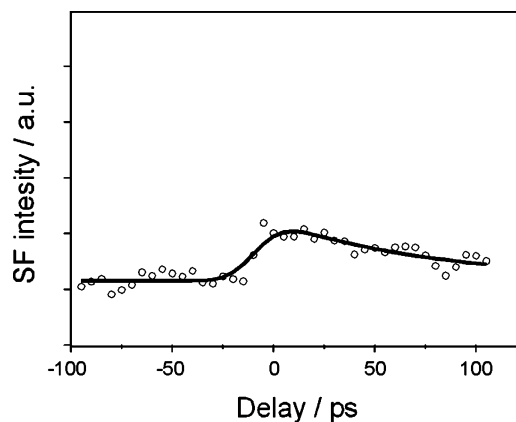


**Figure 4.** Transient SFG spectra of the CO stretching region at delay times of  $-80$ ,  $0$ , and  $70$  ps.

at a given potential required 20–60 min, while the recording of CV in the entire potential range required less than 1 min.

Figure 3 shows the temporal profile of the intensity change in the SFG signal at the peak of the  $\nu_{\text{CO}}$  mode ( $2055\text{ cm}^{-1}$ ) at 0 mV induced by visible pump pulse irradiation. The solid line is the least-squares fit using a convolution of Gaussian function for the laser profile (fwhm = 20 ps) and a single exponential function for the recovery profile. The SFG signal fell into a minimum within the laser pulse width and recovered to the initial value with a time constant of 75 ps. There was a linear correlation between the pump fluence and the intensity decrease induced by the pump pulse, and no intensity change was observed when the pump fluence was less than that of the SFG probe (532 nm) pulse.

Figure 4 shows transient SFG spectra at delay times of  $-80$ ,  $0$ , and  $70$  ps. The spectrum observed at  $-80$  ps, that is, 80 ps before pumping, was the same as those observed without pumping (Figure 2), indicating that the irradiation-induced changes in the spectra were restored during the 0.1-s interval of pump pulse repetition (10 Hz). Maximum change in spectral



**Figure 5.** Temporal profile of the SFG signal intensity at  $1980\text{ cm}^{-1}$  at a potential of 0 mV. The solid line is the result of a least-squares fitting (see text).

features was observed at a delay time of 0 ps. The peak height of the SFG peak was decreased, the peak position was slightly shifted to a lower wavenumber, and the peak was broadened. The values of fwhm derived from the fits are  $\sim 20$  and  $\sim 25\text{ cm}^{-1}$  at delays of  $-80$  and  $0$  ps, respectively. Furthermore, a new peak appeared at around  $1980\text{ cm}^{-1}$ .

The temporal profile of the intensity change at the new peak ( $1980\text{ cm}^{-1}$ ) induced by visible pump pulse irradiation (Figure 5) clearly shows that the SFG intensity indeed increased and recovered to the original value. The time constants for the rise and recovery of the SFG signal were the same as those of the intensity change at  $2055\text{ cm}^{-1}$  (Figure 3), showing that the decrease of the peak at  $2055\text{ cm}^{-1}$  was accompanied by the increase of the peak at  $1980\text{ cm}^{-1}$ .

One possible origin of the new peak is the  $\nu = 1 \rightarrow 2$  transition (hot band) of stretch vibration of CO adsorbed on the Pt surface. Due to a vibrational anharmonicity, a hot band will give rise to a new peak in a lower wavenumber region than the fundamental peak ( $\nu = 0 \rightarrow 1$ ). The frequency shift from the initial CO stretching band to the new broad peak observed in the present study was, however,  $\sim 88\text{ cm}^{-1}$ , which was much larger than the previously reported value for CO on a Pt surface ( $\sim 30\text{ cm}^{-1}$ )<sup>28</sup> and in the gas phase ( $\sim 27\text{ cm}^{-1}$ ).<sup>29</sup> Thus, it is unlikely that the new peak is due to excitation of the hot band generated by pump pulses.

Another possible reason for the appearance of the new peak is the transient site migration of CO on the Pt surface. It has been reported that CO adsorbed on a multibonded<sup>30</sup> or asymmetric bridge site<sup>31</sup> gave a peak at  $\sim 1980\text{ cm}^{-1}$ . Thus, it is reasonable to consider that the SFG intensity decrease and the appearance of a new peak were caused by reversible site migration of CO on the Pt surface from the atop site to a multibonded or asymmetric bridge site induced by intense pump pulse irradiation. The similarity in the temporal behaviors of SFG intensity at  $2055$  and  $1980\text{ cm}^{-1}$  supports this model.

The low-frequency shift and the broadening of the CO spectra at a delay of 0 ps suggest that the low-frequency modes of adsorbed CO, that is, stretching, frustrated rotation, and frustrated translation modes of Pt–CO, were thermally excited by pump pulses, as reported by Bonn et al.<sup>32</sup> Thus, it is concluded that the transient site migration of adsorbed CO on the Pt surface was caused by a transient rise in the surface temperature of Pt induced by pump pulses.

Since there is a possibility that CO migration was induced by electronic excitation by pump pulses coupled with a small and short lattice temperature jump,<sup>33</sup> further detailed pump–

probe experiments using different excitation wavelengths are now in progress.

In conclusion, TR-SFG measurements were carried out on a Pt electrode/electrolyte interface covered with a CO monolayer under irradiation of picosecond visible pulses. We observed transient reversible migration of CO molecules on the Pt surface under electrochemical conditions. Upon visible pump pulse irradiation, the population of on-top CO decreased immediately followed by an increase of multibonded CO due to a transient temperature jump at the surface. This is the first report presenting results that show a transient reversible migration of CO molecules adsorbed on a Pt surface under electrochemical conditions.

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