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Adsorption and decomposition of formic acid (DCOOD) on NiO(111) and Ni(111) surfaces probed by SFG

A. Bandara, J. Kubota, A. Wada, K. Domen, C. Hirose*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
(Fax: +81-45/924-5276, E-mail: chirose@csd.res.titech.ac.jp)

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Abstract. Adsorption and decomposition of formic acid (DCOOD) on NiO(111)/Ni(111) and Ni(111) surfaces under ultrahigh vacuum (UHV) conditions and the steady flow of DCOOD gas were investigated by sum-frequency generation (SFG) spectroscopy. Formates adsorbed via two carbonyl oxygen atoms were produced by the adsorption and the species on the oxide surface had two orientations in UHV; the species which decomposed at around 300 K was tilted from the surface normal and that decomposing at ∼ 400 K was vertical to the surface. We induced the decomposition on the oxide surface by irradiation with picosecond 1064 nm pulses which caused the surface temperature to jump by ∼ 300 K with ∼ 100 ps decay time. The transient temperature jump transformed reversibly the stable formates to the monodentate formate adsorbed via one oxygen atom and the decomposition occurred at 100 K above the onset temperature 275 K of the transformation. The transformation was ascribed to the shift of chemical equilibrium due to the laser induced temperature jump. The energy difference between the two species and the activation energy for the decomposition of monodentate formate were derived.

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The understanding of the dynamics of surface chemical reactions at the microscopic level is the major subject of surface chemistry and the observation of chemical species produced during a reaction at surfaces is vital to the characterization of dynamical pathways of the reaction in which the adsorbed molecules or atoms react and desorb from or are incorporated into the surface, and the presence of short-lived intermediate species has been postulated for most surface reactions. Intensive investigations have been carried out in the past few decades using conventional surface vibrational spectroscopic techniques such as infrared reflection absorption spectroscopy (IRAS) and high resolution electron energy loss spectroscopy (HREELS) [1–5], but clear evidence for the species participating in the reactions has been lacking.

A versatile way to elucidate such an evidence is the use of laser irradiation. Lasers enabled us to initiate a reaction in a well-defined and well-controlled fashion and the use of such spectroscopic techniques as time-resolved IRAS using pulsed infrared sources, and sum-frequency generation (SFG) spectroscopy has made it possible to probe the surface species participating in a reaction without desorption [6–9]. These techniques made possible not only the characterization of surface species but also the probing of the reaction in real time to get information on the energy flow in the events. A major achievement of this kind of experiment has been the measurement of relaxation times of vibrational energy from adsorbed molecules to surfaces [10–14].

We have recently succeeded in performing an experiment aimed at the characterization of chemical reactions on surfaces [15]. The basic idea is that temperatures of several hundreds to a thousand Kelvin can be realized for only a short period of time on surfaces by the irradiation of ultrashort laser pulses, and the density of the reaction intermediates produced under such conditions can be much higher than that occurring in conventional experiments such as temperature programmed desorption (TPD) [16–18]. The extremely short rise and rapid fall of surface temperature realizes an instantaneous accumulation of transient species enabling us to detect and follow the time course of the species by SFG spectroscopy. In the experiment, the thermal decomposition of formate (DCOO) on the Ni(111) and NiO(111) surfaces was induced by irradiation with picosecond 1064 nm laser pulses, which induce a transient temperature jump of ∼ 300 K.

The decomposition of formic acid on single crystal metal and oxide surfaces has been investigated for the past three decades using TPD and conventional vibration spectroscopies such as HREELS and IRAS [19–26], and the presence of surface formate species either on the adsorption of formic acid at room temperature or on annealing surfaces with adsorbed formic acid at low temperatures has been verified. These *stable* formates are adsorbed at two carbonyl oxygens either to two surface atoms (bridged configuration) or to one surface atom (bidentate configuration) and decompose at elevated temperatures to yield H_2 and CO_2 (dehydrogenation) or H_2O and CO (dehydration) as desorbates. We previously in-

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* Corresponding author. E-mail: chirose@csd.res.titech.ac.jp

vestigated by IRAS the thermal decomposition of formic acid over the NiO(111) surface under heavy flow of formic acid and revealed that monodentate formate, which is bonded to the surface via the oxygen atom of the C−O bond of carboxyl group instead of two oxygen atoms of the carbonyl group, appeared when the decomposition started [27, 28]. However, the experiment allowed us neither to verify whether the new species was the intermediate of the reaction or produced by secondary or side reactions, nor to elucidate the dynamical behavior of the surface species by the static IRAS measurement. The pump–probe experiment using a combination of the laser-induced temperature jump and probing by time-resolved SFG spectroscopy provided the lacking information.

This paper describes the results obtained for the DCOO/NiO(111) system, and another article in this issue [29] gives a detailed account of the SFG spectroscopy and the results for the DCOO/Ni(111) system.

1 Experimental

Details of the optical setup for SFG and the ultra high vacuum (UHV) chamber used for the present experiments are described in a separate paper in this issue [29].

A clean Ni(111) surface, obtained by repeated cycles of Ar ion bombardment followed by annealing at 1100 K with the cleanliness and orderliness of the surface being confirmed by AES and LEED observations, respectively, was oxidized by repeated cycles of dosing with 1000 L ($1\,\mathrm{L} = 1\times10^{-6}$ Torr s, 1 Torr = 133 Pa) of oxygen at 570 K and annealing at 650 K in vacuum [26–28]. Three such cycles gave sharp LEED spots proving the formation of the (2×2)-NiO(111) phase. The peak-to-peak ratio of 1.75 of the AES $\mathrm{O_{KLL}}$ peak at 510 eV with respect to the $\mathrm{Ni_{LMM}}$ peak at 848 eV indicated the formation of about 5 monolayers of oxide [21–23]. The adsorption sites on the resulting oxide surface were dominated by fully oxidized sites as proved by the IRAS and SFG spectra of the surface adsorbed by CO as reported previously [26]. Commercial formic acid (DCOOD) with 99.5% purity was purified by repeated freeze–pump–thaw cycles prior to use. DCOOD is known to adsorb as formate above 160 K on the NiO(111) [27, 30, 31] and above 200 K on the Ni(111) surfaces [29] with bidentate and bridged configurations, respectively.

The measurements under UHV were made at various coverages and temperatures while those under irradiation with picosecond laser pulses were carried out at various temperatures and under an atmosphere of 3×10^{-5} Pa formic acid (DCOOD) to maintain a constant coverage.

2 Results and discussion

2.1 *Adsorption and decomposition of formic acid under UHV conditions*

We first describe the results of the SFG measurements of the formate-covered NiO(111) and Ni(111) surfaces performed under UHV conditions. The spectra observed for the NiO(111) and Ni(111) surfaces, dosed by DCOOD to saturation at 250 K, are shown in Fig. 1a and b, respectively. The signal intensities obtained by using the *p*-polarized visible and *p*-polarized infrared (IR) pulses [denoted as (*pp*) polarization combination] and those observed by the *s*-polarized visible and *p*-polarized IR pulses [denoted as (*sp*) polarization combination] are plotted as open circles. The solid lines drawn through the data points are the theoretical spectra obtained by simulation [29, 32]. The C−D stretching bands at 2160 cm^{-1} for the DCOO/NiO(111) and 2196 cm^{-1} for the DCOO/Ni(111) systems are in line with our previous IRAS observation where the appearance of characteristic vibrational bands proved the presence of bidentate and bridged formates on the NiO(111) and Ni(111) surfaces, respectively [27, 29, 32]. A previous paper on the SFG spectra of formate on clean and oxide-layered Ni(100) surfaces reported that the signals due to the C−H stretching mode of formate were observed only for the (*pp*) polarization combination [33], and a vertical orientation of the C−H bond was postulated for both surfaces. The present observation of signals for both the (*pp*) and (*sp*) combinations on the DCOO/NiO(111)/Ni(111) system is thus exceptional. The SFG signal derives from the second-order susceptibility which in turn is the product of the Raman polarizability ten-

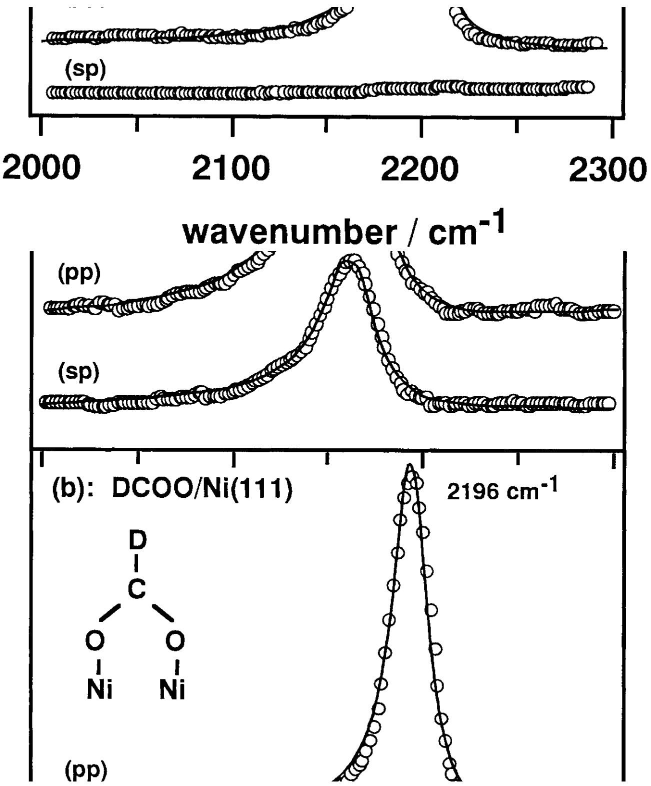

Fig. 1a,b. SFG spectra in the C−D stretching regions of the DCOO saturated NiO(111)/Ni(111) (**a**) and Ni(111) surfaces (**b**) at 250 K under UHV conditions. The spectra obtained by using the (*pp*) and (*sp*) polarization combinations are plotted as *open circles*. *Solid lines* are the theoretical fits as described in the text sor and the transition moment of the vibrational mode. Taking the C−D axis as the *c* axis of the molecule-fixed (*abc*) coordinate system and assuming C_∞ symmetry for the C−D bond, the Raman tensor for the C−D stretching mode is dominated by α_{cc} [32–34] and the transition dipole vector lies along the *c* axis. Thus the SFG polarizability is dominated by β_{ccc} component and the SFG signal is generated only when the electric fields of the infrared and visible light beams have components along the C−D bond. Incidentally, the observed SFG signals were p and s polarized for the (*pp*) and (*sp*) combinations, respectively, indicating that the surface orientation of the C−D bonds were two-dimensionally isotropic [32]. The appearance of SFG signals for both the (*pp*) and (*sp*) combinations implies that the C−D bond on the NiO(111) surface is tilted from the surface normal as shown in the inset of Fig. 1a. This is explained by noting that the NiO(111) surface is known to be the (2 × 2) oxygen-terminated one with oxygen anions (O^{2-}) lying on the top layer. The adsorption sites Ni^{2+} are then located along the slopes of the (100) microfacets and the formates with the molecular plane vertical to the (100) face are tilted from the (111) face accordingly.

The thermal stability of the formate was investigated by TPD and SFG spectroscopy. Shown in Fig. 2a are the TPD spectra obtained from the NiO(111) surface after exposure to the saturation coverage of formate at 250 K. The corresponding data for the Ni(111) surface are given in [29]. One sees from Fig. 2a that the surface formate decomposed to D_2 and CO_2 at 340–390 K and 520 K and to CO and D_2O at 415 and 520 K [26]. Figure 2b compares the SFG spectra observed at various substrate temperatures for the DCOO-saturated NiO(111) surface under UHV. The measured surfaces were prepared by the dosing to the full coverage by DCOOD molecules at 150 K and heating to the measured temperature, and the spectra obtained for the (*pp*) and (*sp*) polarization combinations are shown on the left and right hand sides, respectively. The vibrational resonances observed on the surface at 150 K, with the signal for the (*pp*) combination having a broad band peaked at around 2200 cm^{-1} and tailed to about 2240 cm^{-1} and that for the (*sp*) combination displaying two bands peaked at 2200 and 2225 cm^{-1}, are probably due to the C−D stretching modes of physisorbed formic acid and multilayer. When the temperature was raised to 200 K, the above bands almost disappeared and a new band developed at 2160 cm^{-1}. The frequency is characteristic of the C−D stretching mode of bidentate formate and the appearance reflects the dissociation of DCOOD to DCOO and D. The signals grew up to 250 K, but, on further heating to 350–400 K, the signal for the (*sp*) combination disappeared and only the signal for the (*pp*) combination remained, though weakened, and this too disappeared at higher temperatures.

Referring to the TPD results (Fig. 2a), we can postulate that there exist two types of formates on the surface: ones that have the C−D bond tilted from the surface normal and started to decompose at ∼ 250 K and others having the C−D bond vertical to the surface, which started to decompose at ∼ 400 K. However, the present data alone cannot answer the question of whether the two types of formates were produced

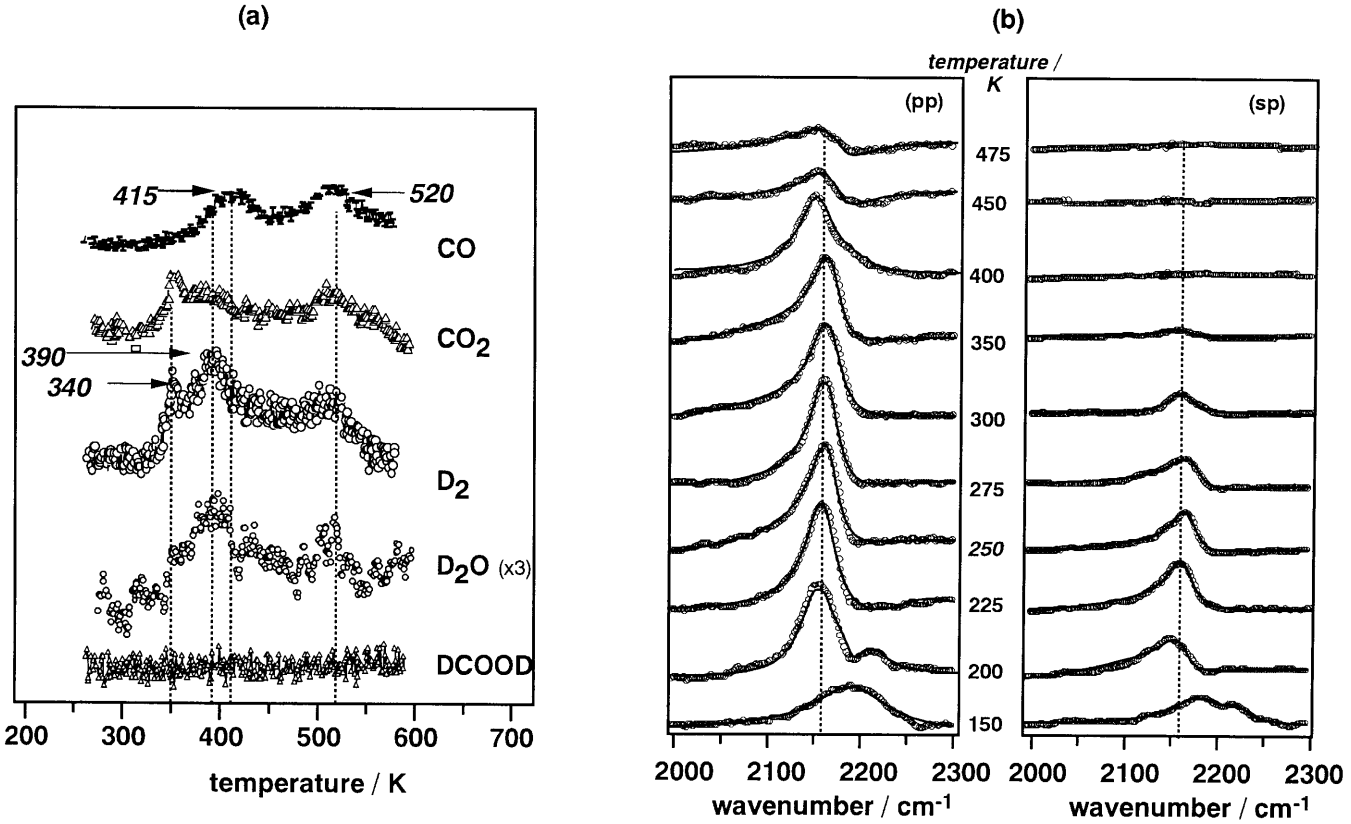

Fig. 2a,b. Temperature programmed desorption (TPD) signals of the DCOO-covered NiO(111)/Ni(111) surface (**a**) and temperature-dependent SFG spectra observed on the DCOO-covered NiO(111) surface for the (*pp*) and (*sp*) polarization combinations (**b**). The surface was first exposed to the saturation coverage of DCOOD at 150 K and annealed to the measured temperatures together at the time of dissociation or whether the formates which survived the first decomposition changed their orientation afterwards.

2.2 *Dynamics of decomposition of formic acid (DCOOD) on* NiO(111) *under irradiation with picosecond laser pulses*

We now proceed to describe the results observed on inducing a pulsed temperature jump to the system under continuous flow of DCOOD. As described in [29], the surface and adsorbed molecules do not resonate with the light of 1064 nm wavelength except for the production of hot carriers in the bulk. Thus a temperature jump of about 300 K was the result of the irradiation with the 1064 nm pulses.

Under UHV conditions, the irradiation of the formate-saturated surfaces caused the SFG band at 2160 cm^{-1} to disappear during the frequency scan indicating the decomposition or desorption of surface formates presumably by the intermittent and more than 100% increase of the pulse energy. But the situation changed when the NiO(111)/Ni(111) surface was kept under the steady flow of DCOOD at 3×10^{-5} Pa, measured by a BA gauge at some distance downstream from the surface. Under this condition, the SFG signals stayed the same.

Shown in Fig. 3 are the SFG spectra in the C$-$D stretching region obtained from the DCOO-covered NiO (111) surface which was irradiated at various substrate temperatures. The spectra observed at delay times of -100 ps, 0 ps (implying actually a delay time of $\sim$ 20 ps when maximal spectral changes were observed), and $+100$ ps are shown for each substrate temperature, and the SFG signals obtained by using (*pp*) combination, shown in Fig. 3a, were *p*-polarized and those obtained by using (*sp*) combination, shown in Fig. 3b, were *s*-polarized. The irradiation induced no signal change when the substrate temperature was below 250 K but there was an apparent change when the substrate temperature exceeded 275 K. However, the spectra observed at -100 ps delay time, that is, 100 ps before the pumping, were the same as those observed without the pumping, indicating that the irradiation-induced changes were restored during the 0.1 s interval of the pulse repetition. When the delay time was 0 ps, the 2160 cm^{-1} peak weakened and a new peak appeared at 2190 cm^{-1}, which was assigned to the ν_{CD} of monodentate formate [15], and, when the surface temperature was 475 K, the 2190 cm^{-1} peak was present even at -100 ps delay time indicating that the formation of the species was activated by the temperature. The resonance peak of the C $=$ O stretching band, observed on the Ni(111) surface [29], was not observed, and the C $=$ O bond of the monodentate formate on the oxide surface was postulated to lie parallel to the surface. One notes that the intensity of the vibrational peak at 2160 cm^{-1}, which was assigned to the C$-$D stretching band ν_{CD} of bidentate formate [15], for the (*sp*) combination was considerably weaker than that observed for the (*pp*) combination. It is thus suggested that the C$-$D bond of the biden-

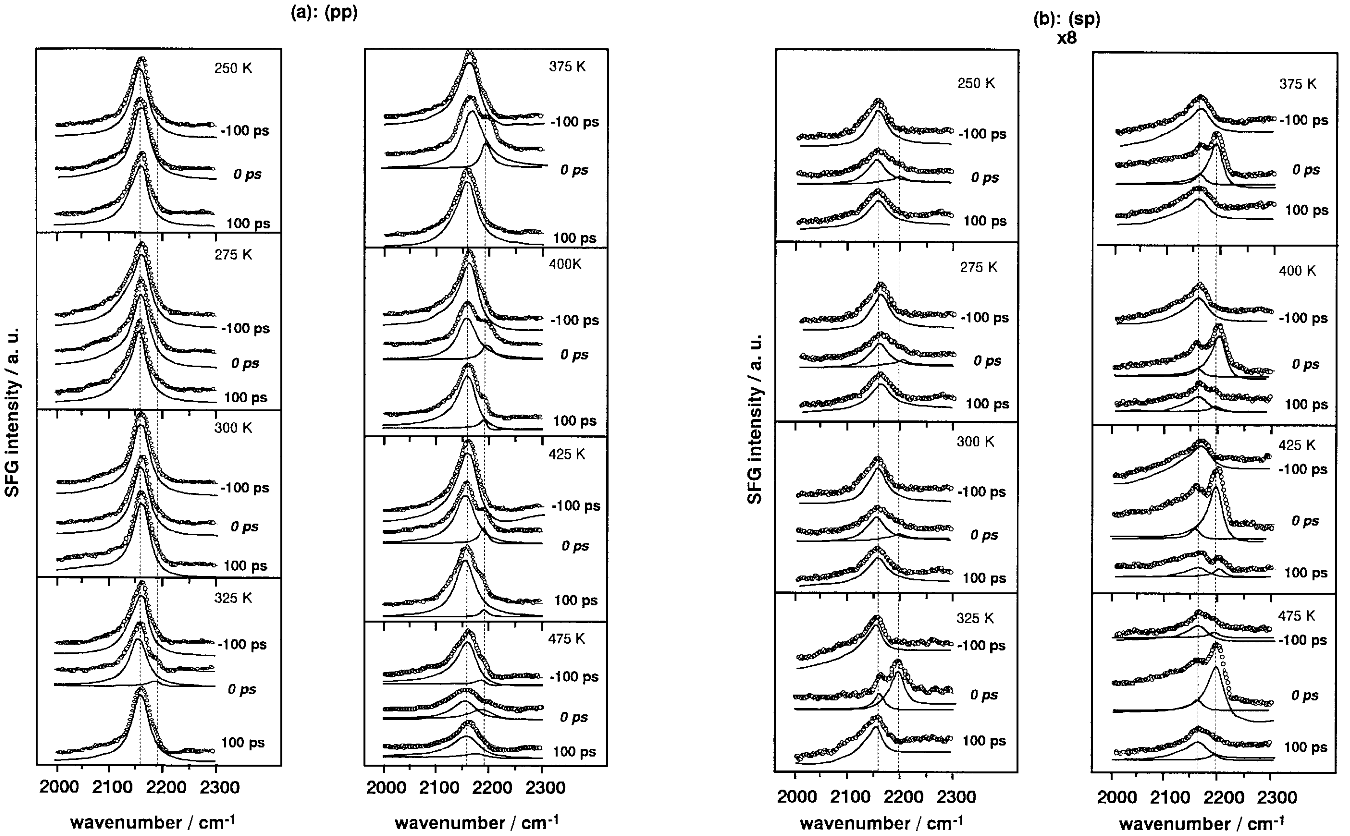

Fig. 3a,b. SFG spectra obtained at different delay times on the DCOO/NiO(111)/Ni(111) system under the irradiation of 1064 nm pump pulses of 10 mJ/pulse energy and at various substrate temperatures. The surface was under the steady flow of DCOOD at 3×10^{-5} Pa. The spectra observed for the (*pp*) and (*sp*) polarization combinations are shown in **a** and **b**, respectively. *Solid lines* are theoretical profiles for the ν_{CD} bands (see text for details) tate formate under steady flow remained similar to that in UHV at relatively low substrate temperature and was tilted from the surface normal. On the other hand, the intensity of the transient 2190 cm^{-1} peak for the (*sp*) combination is considerably higher than that for the (*pp*) combination and thus the C$-$D bond of the monodentate formate should be pointed significantly away from the surface normal. The observed spectra were fitted to the squares of the nonlinear susceptibility tensor having two vibrational resonances at 2160 and 2190 cm^{-1}, $|\chi_{\rm NR}+\chi_{2160}/(\omega_{\rm IR}-2160+{\rm i}\Gamma_{2160})+\chi_{2190}/(\omega_{\rm IR}-2190+{\rm i}\Gamma_{2190})|^2$ (where $\omega_{\rm IR}$ is the frequency in cm^{-1} of the IR pulses, χ_{2160} and χ_{2190} are the amplitudes, and Γ_{2160} and Γ_{2190} are the HWHM widths of the two vibrational bands, respectively) [29, 32]. Thus derived values of parameters are listed in Table 1 along with the values derived for the DCOO/Ni(111) system described in [29]. Hypothetical component signals $|\chi_{\rm NR}+\chi_{2160}/(\omega_{\rm IR}-2160+{\rm i}\Gamma_{2160})|^2$ and $|\chi_{\rm NR}+\chi_{2190}/(\omega_{\rm IR}-2190+{\rm i}\Gamma_{2190})|^2$ as obtained by the fitting are shown by the solid lines with shifted baselines. The asymmetric shape of the component signals is due to the vibration-nonresonant nonlinear term $\chi_{\rm NR}$. Temperature-dependent shifts of peak frequency were negligible for all the $\nu_{\rm CD}$ bands observed. As described in [29], only the (*pp*) combination gave SFG signals and no signal was observed for the (*sp*) combination on the Ni(111) surface and the vibrational resonance due to the $\nu_{\rm CD}$ band of the bridged formate was observed at 2196 cm^{-1}. The 2196 cm^{-1} signal weakened and a new signal due to the C = O stretching mode of monodentate formate appeared at 1718 cm^{-1} at the instant of the irradiation with the 1064 nm laser pulses.

The observed signal-to-noise ratio was high enough to allow us to perform the delay-scan experiment. The results are shown in Fig. 4, where the intensities of the SFG signals at 2160 and 2190 cm^{-1} are plotted against the delay times imposed between the pump pulse and the pulses for the SFG measurement. The measurements were made for the (*pp*) combination and at various substrate temperatures. The results confirmed the above-stated features that no irradiation-induced change was observed below 250 K and the change became appreciable when the surface was above 275–300 K. In addition, both the irradiation-induced intensity loss at 2160 cm^{-1} and the transient signal at 2190 cm^{-1} recovered

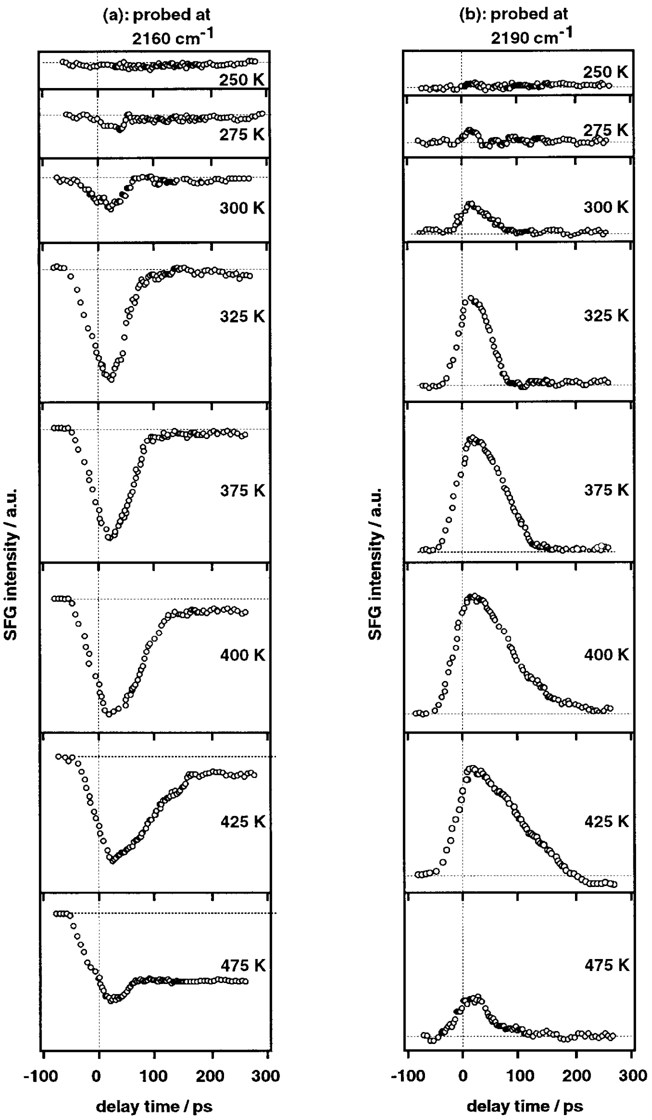

Fig. 4a,b. Changes by delay time of the SFG signals at 2160 (**a**) and at 2190 cm^{-1} (**b**) of the DCOO-covered NiO(111)/Ni(111) surface at various substrate temperatures. The surface was under the steady flow of DCOOD at 3×10^{-5} Pa, and the (*pp*) polarization combination was used

Table 1. The values of parameters derived from the fitting of the SFG spectra of DCOO/NiO(111) and DCOO/Ni(111) systems at various temperatures

DCOO/NiO(111)[a]							DCOO/Ni(111)[b]				
Temp. /K	delay /ps	$\chi^{\rm NR}$	$\chi^{\rm R}_{2160}$	Γ_{2160}	$\chi^{\rm R}_{2190}$	Γ_{2190}	Temp. /K	delay /ps	$\chi^{\rm NR}$	$\chi^{\rm R}_{2196}$	Γ_{2196}
	−100	0.21	3.82	18.72	–	–		−100	0.121	3.59	11.32
300	0	0.24	3.81	18.53	–	–	250	0	0.112	3.58	11.38
	100	0.23	3.81	18.24	–	–		100	0.081	3.58	11.28
	−100	0.17	3.71	17.89	–	–		−100	0.112	3.59	11.32
325	0	0.21	3.51	18.12	1.12	10.42	275	0	0.101	3.47	11.46
	100	0.23	3.72	18.11	–	–		100	0.120	3.60	11.27
	−100	0.12	3.72	19.49	–	–		−100	0.091	3.74	11.72
375	0	0.29	3.47	20.12	1.32	11.62	300	0	0.080	3.40	11.89
	100	0.12	3.72	19.49	–	–		100	0.101	3.66	11.60
	−100	0.18	3.86	21.11	–	–		−100	0.036	3.42	12.24
400	0	0.26	3.49	21.50	2.18	11.88	320	0	0.054	3.13	12.91
	100	0.18	3.60	20.51	0.12	9.32		100	0.065	3.25	12.76

[a] The $\omega_{\rm IR}$ were fixed at 2160 and 2190 cm^{-1}

[b] $\omega_{\rm IR}$ was fixed at 2196 cm^{-1}

within 100–200 ps at the temperatures below 375 K but not fully at the temperatures higher than 400 K. The similarity in the recovery features suggested that the bidentate formate transformed reversibly to monodentate formate and that the two species were in thermal equilibrium. The unrecovered intensities at 2160 cm^{-1} at high substrate temperatures are ascribed to the loss of surface formate by thermal decomposition. Similar behavior to that observed at 2160 cm^{-1} on the present DCOO/NiO(111)/Ni(111) system was observed at 2196 cm^{-1} on the DCOO/Ni(111) system in the temperature region of 275–335 K indicating the occurrence of similar processes on the two surfaces, but the temperature dependence was much steeper on the Ni(111) surface.

Postulating an equilibrium between the bidentate and the monodentate formates on the NiO(111) surface, equilibrium constants K at each temperature were derived from the relative amounts of the monodentate formate with respect to the bidentate formate, which can be estimated from the χ_{vib} values for the two SFG bands derived from the above-described fitting. (See [29] for the formulas of the analysis.) The slope of the plots of thus estimated equilibrium constants (in logarithmic scale) against the reciprocals of maximum temperature gave as the energy difference between the two kinds of formates a value of 19 ± 5 kJ/mol. Furthermore, the activation energy of about 30 ± 10 kJ/mol, which is in fair agreement with previously derived value [27], was obtained for the decomposition of monodentate formate from the integration of temporal profiles measured in the 300–500 K temperature region. The method was not applicable to the Ni(111) surface, since the ν_{CD} bands there overlap and the temperature dependence was anomalously large.

3 Summary

The decomposition of DCOO on Ni(111) and NiO(111)/Ni(111) surfaces has been investigated by TPD and conventional SFG spectroscopy under UHV conditions and by combining SFG spectroscopy and the laser-induced temperature jump under a steady flow of DCOOD. The investigation under UHV conditions revealed the occurrence of two types of formates; the ones decomposing at lower temperatures were tilted from the surface normal while the others, which decomposed at higher temperatures, were oriented vertical to the Ni(111) surface. The time-resolved observation of the surfaces under the steady flow revealed that thermal decomposition of formates on the NiO(111) surface was preceded by the reversible transformation between the stable bidentate formate and unstable monodentate formate presumably by the shift of chemical equilibrium caused by the laser-induced pulsewise jump of the surface temperature. The energy difference between the bidentate and monodentate formates and the activation energy for the decomposition of monodentate formate were derived as 19 ± 5 and 30 ± 10 kJ/mol, respectively.

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