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SFG Spectroscopy of CO/Ni(111): UV Pumping and the Transient Hot Band Transition of Adsorbed CO

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A UV excitation by a picosecond pulse at 266 nm induced an unusual shoulder on the $\nu_{CO} = 1 \leftarrow 0$ resonance peak of CO/Ni(111) monitored by sum-frequency generation (SFG) of visible and IR pulses. The observed line shape was reproduced by the use of a dipole-dipole interaction model with the coherent potential approximation (CPA) where the hot band transition with a population ratio of 0.3 to 0.7 ($v = 1$ to $v = 0$) was assumed. Neither the transition to the two-phonon bound state nor the coupling with the low-frequency phonon modes explained the observed changes. The shoulder appeared only during the UV excitation, which indicated that the electronically driven excitation, presumably by the hot electrons generated by the irradiation, dominated the process. As possible mechanisms, the involvement of an intermediate negative ion resonance state and/or the non-adiabatic coupling of electronic states with C–O stretching mode were considered.

Photo-induced processes at adsorbate-metal surfaces, especially for the CO-metal systems, have been studied intensively because of their fundamental roles in surface photochemical reactions.[1] As for the CO/Cu systems under the irradiation of a sub-picosecond visible (2.19 eV) pulse[2] and a picosecond UV (4.29 eV) pulse,[3,4] a transient shift and a change of the infrared (IR) band shape of the C–O stretching band were observed and no substantial difference is reported between the results of visible and of UV pumping. To interpret the results, the vibrational relaxation and dephasing via the frustrated translation mode were postulated. Furthermore, nonadiabatic energy transfer through vibration–electron coupling was suggested from the experiment with a resonant IR pumping.[5] For the CO/Ru system pumped by an 800 nm femtosecond pulse,[6] a peak shift and a broadening of C–O stretching band were observed on time-resolved SFG spectra. The observed changes were interpreted as the dephasing via the thermally excited frustrated modes. For the CO/Pt systems with a resonant IR pumping, a red-shifted and broadened single peak was observed on the C–O stretching band when it was probed by infrared reflection-absorption spectroscopy (IRAS).[7,8] The electron-hole pair damping mechanism for the vibrational relaxation was proposed, and UV- and visible-induced excitation of the coupled anharmonic lattice oscillators as well as the possibility of two-phonon bound state (TPBS)[9–11] were discussed.[12]

The interpretation of the vibrational spectrum of surface species is not straightforward because of the dipole-dipole coupling when the dipole moment of the species is large, which is the case for CO molecule.[13,14] The lineshape of the C–O stretching band has been studied theoretically on some of the relaxation models,[15–21] and the IRAS results of overtone and combination tones of the C–O stretching mode adsorbed on Ru have been related to the two-dimensional delocalization/localization picture of molecular vibrations.[22–24] One of the issues is the extent of delocalization of the vibrational excitation, that is, whether we observe a hot band of localized oscillators, a TPBS of partially delocalized oscillators, or a fully delocalized single and broad resonance peak of the phonon band that originates from the C–O stretching vibration.

In this report, we describe the observed feature of the time-resolved vibrational SFG spectrum of the CO/Ni(111) system pumped by picosecond UV radiation (266 nm, 4.7 eV). A significant change in the spectrum was observed with the UV pumping (but not with the visible pumping).[25] The possibilities of coherent artifacts (saturation broadening and four-wave mixing) are discriminated, and we discuss about the vibrational transition (SFG spectrum given by dipole interactions in the regime of coherent potential approximation, two-phonon bound state for the red-shift shoulder, hot band transition) to interpret the observed phenomena.

Experiment and Results

The schematic diagram of the experimental setup is shown in Fig. 1. Tunable picosecond infrared (IR) pulses for the SFG were obtained by difference frequency generation of near-IR and 1064 nm pulses in a $AgGaS_2$ crystal.[26] The near-IR pulses were generated by an optical parametric generator/amplifier which was pumped by the second harmonic output of a mode locked Nd:YAG laser (the pulse width was 35 ps and the repetition rate was 10 Hz). A portion of the 1064 nm output pulses were led to a KDP crystal to generate visible (532 nm) light for the SFG. A part of the 532 nm pulses was led to another KDP crystal to produce the UV pump pulses (wavelength of 266 nm, pulse width of 18 ps, pulse energy of 150 μJ). The IR and

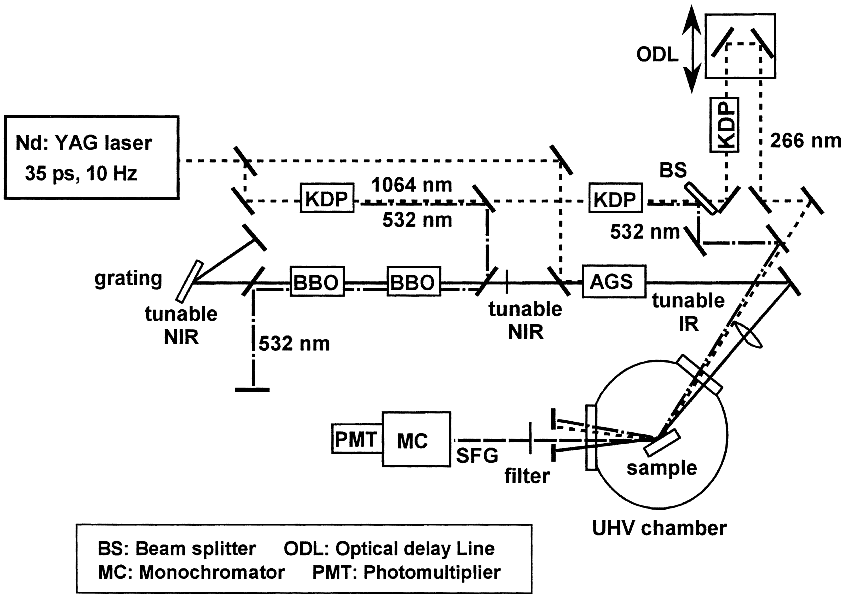

Fig. 1. Schematic diagram for the UV-pump and SFG-probe experiment. The picosecond tunable IR pulses for SFG were generated by the combination of optical parametric generation and amplification (OPG/OPA) and difference-frequency generation (DFG). The UV pulses for pumping were obtained by the fourth harmonic generation of the output of mode-locked Nd:YAG laser. The sample was held inside the ultra high vacuum (UHV) chamber (base pressure ~1 × 10^{-8} Pa).

attenuated visible pulses (wavelength of 532 nm, pulse width of 25 ps, pulse energy of lower than 100 μJ) for SFG were overlapped on the sample surface at an incident angle of about 75°. The IR pulses (FWHM was 3 cm^{-1} and pulse duration was 18 ps at 2000 cm^{-1}) with the pulse energy of about 80 μJ at 2000 cm^{-1} were mildly focused at the surface to the diameter of about 3 mm. The visible pulses with the diameter of about 5 mm were without focusing. The diameter of the UV pulses was also about 5 mm. All the three lightbeams were overlapped to maximize the SFG signal. The generated SFG photons were detected by a photomultiplier tube after passing through optical filters and a monochromator. In the time-resolved measurements, an optical delay line was used for the timing of the pump and probe pulses.

The experiment was carried out in an ultra high vacuum (UHV) chamber having the base pressure of ~1 × 10^{-8} Pa. The chamber was equipped with a four-grids analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a quadrupole mass spectrometer for TPD measurements. The used disk of Ni(111) single crystal had one mm thickness and 10 mm diameter. The disk was attached to a liquid nitrogen-cooled sample holder by two Ta wires, and the sample temperature was variable between 130 and 1300 K. The crystal surface was cleaned by repeated cycles of Ar ion bombardment at 300 K and annealing at 1100 K. The cleanness and long-range structure after the treatments were checked by AES and LEED, respectively. The SFG measurements under the UV pumping were performed at the saturation coverage $\theta_{\mathrm{CO}} = 0.57$, θ_{CO} being the ratio of the number of CO molecules with respect to that of the Ni atoms on the outermost layer. This condition is realized in the atmosphere of 1 × 10^{-5} Pa CO. The sample temperature was 250 K.

The SFG spectra were observed using the p-polarized visible and p-polarized IR pulses. No signal was observed with the s-polarized visible pulses. The transient jump of the surface temperature due to the irradiation by the UV, visible, and IR pulses was estimated to be not higher than several tens K, where the maximum pulse energy was 2.5 mJ/pulse of visible light into the area of 5 mm diameter. The estimation was obtained by solving the heat diffusion equation and also from our previous experimental data.[27,28]

The SFG spectra observed with and without UV pumping are shown in Fig. 2 by diamonds and circles, respectively. The resonance peak at 2076 cm^{-1} has been assigned to the stretching mode of CO linearly bonded onto the surface.[29] In our ex-

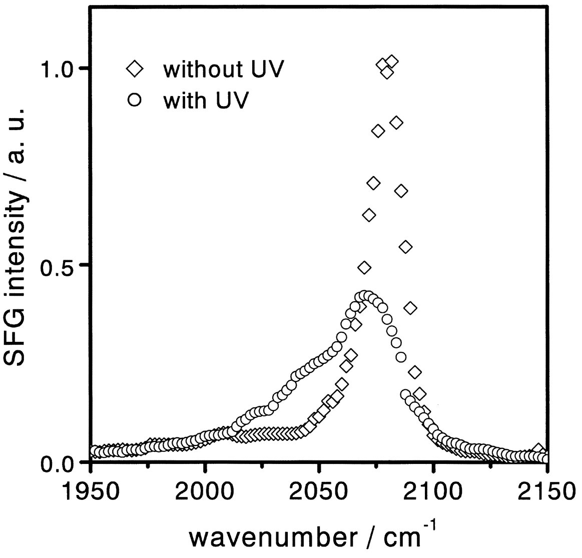

Fig. 2. SFG spectra of CO adsorbed on Ni(111) at 250 K without (circles) and with (diamonds) the irradiation of 266 nm UV pulses having 150 μJ/pulse energy.

periment, the following changes by the UV pumping were observed on the SFG spectrum: (1) The peak height at 2076 cm^{-1} significantly decreased and the full width increased from ~18 cm^{-1} to ~31 cm^{-1} which is the width of main peak derived by the least-squares fit using two Lorentz functions, and (2) a new band (i.e., a relatively broad shoulder) appeared at around 20 cm^{-1} below the main peak. These changes became pronounced with the increase of the UV power. The temporal features of the changes are shown in Fig. 3, where the signal intensities at 2074 and 2058 cm^{-1} are plotted against the delay time of the SFG measurement in Figs. 3a and 3b, respectively. It is seen that there is no tail in the positive delay region. Therefore, (3) the induced changes lasted only during the period of the UV pulse and the lifetime of the UV effect would be shorter than 10 ps.

When the UV pulse was cut and the visible pulse energy was increased by 150 μJ instead of the UV irradiation, the spectral feature was the same as that of the spectrum obtained in low visible pulse energy without UV pumping. At much higher visible fluence of ~1.3 mJ/pulse (and without UV pumping), a change in the spectral feature was barely noticeable (not shown). This was different from the result observed under the UV pumping. In addition, the induced change persisted longer than 100 ps. Such results indicate that the observed change induced by UV irradiation was caused by a nonthermal process different from the process reported in Ref. 6.

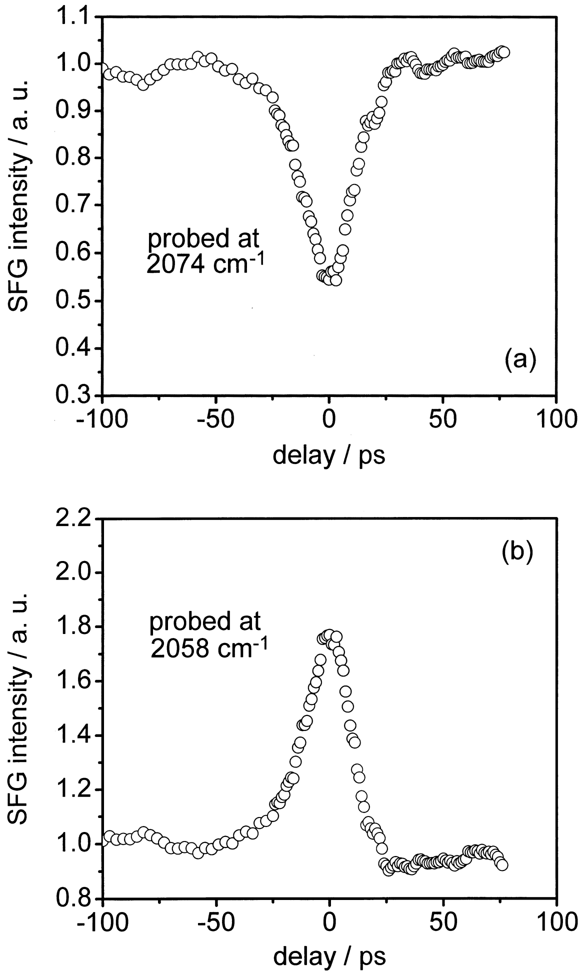

Fig. 3. Temporal recovery profiles of the irradiation-induced changes of the SFG signals of the CO on Ni(111) at 250 K. The irradiation was made by the 266 nm UV pulses with 150 μJ/pulse energy. The signal changes monitored at 2074 cm^{-1} (a) and 2058 cm^{-1} (b) are shown against the delay time from the UV irradiation. Note that the vertical axes are modified and do not comply with that of Fig. 2.

Discussions

A. Coherent Artifacts. **A.1. Saturation Broadening.** As for the broadening under the UV excitation, the Rabi frequency as the measure of saturation broadening will be less than several cm^{-1} when the UV pumping of 150 μJ, into the area of about 5 mm in diameter, is in exact resonance with a transition dipole of 1 D. Because the resonant linewidth of the SFG spectrum is given mainly by the IR transition, it should be less than the saturation broadening of the suppositional UV transition even when a level is shared. We discard the possibility of coherent interaction with the UV light resulting in the broadening.

A.2. Interference of SFG and 4WM Signals. Next we eliminate the effect of a possible coherent interaction to the peculiar shoulder of the spectrum with the UV pumping. Major concern is the four wave mixing (4WM) of the UV, visible and IR lightbeams, which is a third order nonlinearity while the SFG signal is associated with the second order nonlinearity. The SFG signal is at $\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$ and arises via the second order nonlinear susceptibility β(ω_{SFG}, ω_{IR}, and ω_{VIS} are the frequencies of the SFG, infrared, and visible pulses, respectively). The 4WM signal, at the same frequency, arises by the third order nonlinear susceptibility γ: $\omega_{\text{4WM}} = \omega_{\text{IR}} + \omega_{\text{UV}} - \omega_{\text{VIS}}$ and we have the relation $\omega_{\text{UV}} = 2\omega_{\text{VIS}}$ in our experimental setting (Fig. 1). If the SFG and 4WM exist at the same time and are coherent, the overall spectrum may be given by the interference of the two signal amplitudes. This interference pattern is sensitive to the relative phase of the incident waves to be mixed, and the phase is determined by the lengths of the delay lines. The present experiment gave the negative result: no indication of such an interference effect was observed when the delay was scanned. Thus we conclude that the spectrum should be described by the sum of the squares, not by the square of the sum, of the two light fields.

A.3. Contribution of 4WM to the Shoulder of the Spectrum. The polarization of the effective dipole moment of the 4WM (4WM polarization) contains both the vibrational resonant and vibration-nonresonant background (BG) terms like the SFG polarization. The magnitude of the BG term with respect to the vibrational resonance term may become larger than in SFG because the UV photon energy is closer to the electronic transition of the CO/Ni system.

By increasing the BG term, one finds that the dispersion type lineshape of the 4WM becomes significant and that the positive-going peak shows an apparent red shift.[30] However, based on the equation (15.4) in Ref. 30, it is easily shown that the sum of the 4WM signal (with the BG term) and the SFG signal (with no/small BG term) never gives rise to a shoulder of the observed spectrum.

The 4WM signal may exist in the observed signal; if that is the case, it may be simply added to the SFG signal to increase the signal intensity without changing the spectral lineshape drastically. As a remaining possibility, therefore, we analyze the observed new band as the appearance of a different vibrational transition, and the broadening as the scattering processes which are caused by *the absorption of UV radiation by the metal substrate.*

B. Dipole–Dipole Interaction Model. B.1. CPA for SFG Line Shape. In interpreting the observed changes as the appearance of a new vibrational resonance band, we take into account the dipole–dipole interaction of the CO molecules. We performed simulations of the spectrum on the basis of the formalism derived by Persson and Ryberg,[14] who introduced the treatment of coherent potential approximation (CPA) and applied the formula to linear susceptibility of molecule-adsorbed surfaces. We apply the formalism to the expression of the nonlinear dipole moment for SFG produced by a surface-adsorbed molecule "A" as,

$$p_{\mathrm{A}}^{\mathrm{SFG}} \approx \frac{\beta_{\mathrm{A}}(\omega_{\mathrm{IR}}+\omega_{\mathrm{VIS}})}{1+\alpha(\omega_{\mathrm{IR}}+\omega_{\mathrm{VIS}})\tilde{\mathrm{U}}(0)} \cdot \frac{E_{\mathrm{ext}}(\omega_{\mathrm{IR}})}{1+\alpha(\omega_{\mathrm{IR}})\tilde{\mathrm{U}}(0)} \cdot \frac{E_{\mathrm{ext}}(\omega_{\mathrm{VIS}})}{1+\alpha(\omega_{\mathrm{VIS}})\tilde{\mathrm{U}}(0)}, \tag{1}$$

where, $E_{\mathrm{ext}}(\omega_{\mathrm{IR}})$ and $E_{\mathrm{ext}}(\omega_{\mathrm{VIS}})$ are the amplitudes of the external field at frequencies of IR and visible pulses, ω_{IR}, and ω_{VIS} , respectively; $\alpha(\omega)$'s are the linear susceptibilities to be calculated self-consistently under CPA; $\tilde{\mathrm{U}}(0)$ is the Fourier transform of the dipole–dipole interaction at the center of the Brillouin zone $q = 0$; and $\beta_{\mathrm{A}}(\omega)$ is the second order susceptibility of molecule "A". In the case when some of the sites at the surface are also randomly adsorbed by a different molecule "B", the nonlinear dipole is expressed simply as an average of the constituent dipoles $p_{\mathrm{A}}{}^{\mathrm{SFG}}$ and $p_{\mathrm{B}}{}^{\mathrm{SFG}}$ over the concentrations c_{A} and c_{B} of the two molecules. Then the intensity of SFG signal is expressed as,

$$I^{\mathrm{SFG}} = |c_{\mathrm{A}}p_{\mathrm{A}}^{\mathrm{SFG}} + c_{\mathrm{B}}p_{\mathrm{B}}^{\mathrm{SFG}}|^2 \tag{2}$$

with the linear susceptibility α being calculated self-consistently. We assumed the same vibrational resonance scheme for $\beta_{\mathrm{A}}(\omega)$ as that for linear term $\alpha_{\mathrm{A}}(\omega)-\alpha_{\mathrm{e}}$, and the non-resonant BG term was added when necessary. The molecule "B" may be the same molecule as "A" but in its vibrational excited state. When this is the case, both the IR absorption to the higher level and the stimulated emission (with negative susceptibility) to the ground state must be taken into account for "B".[31]

To determine the parameters for dipole–dipole interaction, we measured the SFG spectra of the sample with different mixing ratios of on-top $C^{16}O$ and $C^{18}O$, at the saturated coverage of $\theta_{\mathrm{CO}} = 0.57$; the results are shown in Fig. 4. The observed shifts of the resonance lines led to the value $W/2 \sim 10$ cm^{-1}, where W is the phonon bandwidth. The best fit of the results was obtained when the full linewidth (without dipole interaction) was put as 18 cm^{-1}. As the IRAS linewidth is $\sim$10 cm^{-1}, the present SFG spectral width of $\sim$18 cm^{-1} should include the broadening due to the bandwidth, $\sim$3 cm^{-1}, of IR source. Also the power broadening by IR pulse of less than a few cm^{-1} (for the input power of 80 μJ and pulse duration of 18 ps and for the transition dipole moment of 0.1 D) should be included, and possibly the broadening of $\sim$10 cm^{-1} because of the irradiation by visible pulse as well.[32] As noted in the experimental section, the utmost temperature jump of several tens K as estimated earlier may add the thermal broadening of $\sim$1 cm^{-1}; so we ignore the broadening induced by the temperature rise.

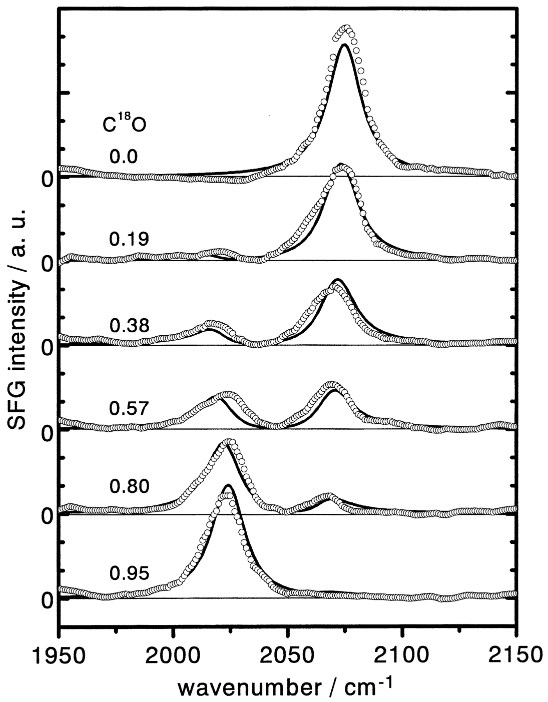

Fig. 4. The SFG spectra of the various isotope mixing ratios of $C^{18}O$ to $C^{16}O$: the portion of $C^{18}O$ were 0.0, 0.19, 0.38, 0.57, 0.80, and 0.95. The open circles are the experimental data after baseline correction and the solid lines are the CPA calculation. The full width of 18 cm^{-1} was assumed in the calculation.

It may be useful to note that, because of the quadratic nature of the SFG spectrum, the integrated area is not a direct measure of the oscillator strength nor of the density of the absorbed molecules, in contrast to the case of IR spectra. For example, the height of an SFG resonance peak decreases, when the corresponding IR integrated intensity is kept constant, to about a half when the full width increases from 18 cm^{-1} to 26 cm^{-1}. The observed decrease of the peak height and broadening of the linewidth, as seen in Fig. 2, should be interpreted by a careful use of model calculations.

B.2. Model of Heterogeneous Mixture. For the origin of the shoulder when the UV pumping is on, we first assumed that the surface was adsorbed by two independent species "A" and "B" (i.e., the CO molecules at two different sites/environments) as in the adsorption of an isotope mixture. This "independent species" model, however, did not give satisfactory simulation of the observed spectra: the simulation failed to reproduce the observed changes of the peak intensity and the linewidth at the same time, and the addition of another signal such as 4WM signal having 1.5 times higher intensity than the SFG signal was needed to attain a reasonable reproduction of observed line shape. The values of parameters used in the calculation were: $W \sim 23$ cm^{-1}, in other words, the new resonance line by species "B" is located at $\sim$23 cm^{-1} below the main resonance line of species “A”, the homogeneous line widths of 33 $\mathrm{cm^{-1}}$ for both “A” and “B” species, and the population ratio of $c_A:c_B = 0.6:0.4$. Although we cannot flatly rule out this “independent species” model, such a strong contribution of the 4WM signal is unlikely and thus the model is rather unreal.

B.3. Two-Phonon Bound State or Hot Band. The remaining and the preferred picture is the assignment of species “B” to the molecules in the vibrational excited ($v = 1$) state of the same “A” species: the UV irradiation induced the vibrational excitation of adsorbed CO molecules. In the study of photo-induced desorption,[33–38] it was suggested that the energy deposited from the laser light into the metal electronic system transfers to the metal-CO vibration modes. It would be natural to consider that the excited electronic system can excite not only the metal-CO vibration modes but also the internal mode of adsorbate, such as the C–O stretching mode. As for the presently investigated system of CO/Ni(111), no photodesorption has been reported to take place, and thus, as an alternative channel of energy transfer, we are interested in the laser-induced vibrational excitation of the non-desorbing molecules.

The possibility of assigning the new band to the transition to two-phonon bound state (TPBS) was eliminated by the following argument. According to the theory by Kimball, Fong and Shen,[39] the transition frequency from a single phonon state to its TPBS at $q = 0$ is red-shifted from the fundamental transition (i. e., the transition from vacuum state to the single phonon state at $q = 0$) by the amount $W + 2\sqrt{\Gamma^2 + (W/2)^2}$ (Γ is the quantity related to the vibrational anharmonicity by $\Gamma = \omega_e x_e$.). This shift should be larger than 40 $\mathrm{cm^{-1}}$ instead of the observed shift of ~23 $\mathrm{cm^{-1}}$ because W ~20 $\mathrm{cm^{-1}}$ in the present system.

Let us now examine the last and preferred postulate that the new band is the hot band transition: hot electrons created by the UV irradiation excited the CO molecules to the $v = 1$ state of the C–O stretching mode. This collisional pumping will induce neither spatial nor temporal coherence in the vibrational oscillations of adsorbed CO molecules throughout the layer. In this sense, the excitation mechanism is localized.

The model proposed by Persson[31] is applicable to this incoherent excitation. The system is basically equivalent to the isotopic mixture with the species “A” having the susceptibility of the $v = 1 \leftarrow 0$ transition and species “B” having the susceptibility of the $v = 2 \leftarrow 1$ transition (the magnitude is doubled if it is a harmonic oscillator). However species “B” now has also the susceptibility which is the negative of that for species “A” since “B” is subject to the stimulated emission by the $v = 0 \leftarrow 1$ transition as well. The out-of-phase polarization induced by the negative susceptibility causes saturation of the absorption and the interaction with the in-phase polarization leads to the peak shift under the dipole interaction. The observed line shape has been reproduced by employing all these factors as shown in Fig. 5, where the values of parameters used are $\omega_e x_e$ of 11.5 $\mathrm{cm^{-1}}$, $c_A:c_B = 0.7:0.3$, and the full widths of 31 $\mathrm{cm^{-1}}$ for the both transitions. There is no report on the value of $\omega_e x_e$ for CO/Ni(111) to our knowledge. The value of ~11.5 $\mathrm{cm^{-1}}$ is small compared to the value 13.3 $\mathrm{cm^{-1}}$ of the isolated CO molecule[40] and it is even smaller than that of CO/Ru system, 18.5 $\mathrm{cm^{-1}}$.[22] However, an even smaller value of 7.5 $\mathrm{cm^{-1}}$ has been reported for $W(CO)_6$,[41–43] and the present assignment (the $v = 2 \leftarrow 1$ transition for the new shoulder) and the value of ~11.5 $\mathrm{cm^{-1}}$ may be acceptable, though the arguments are not decisive.

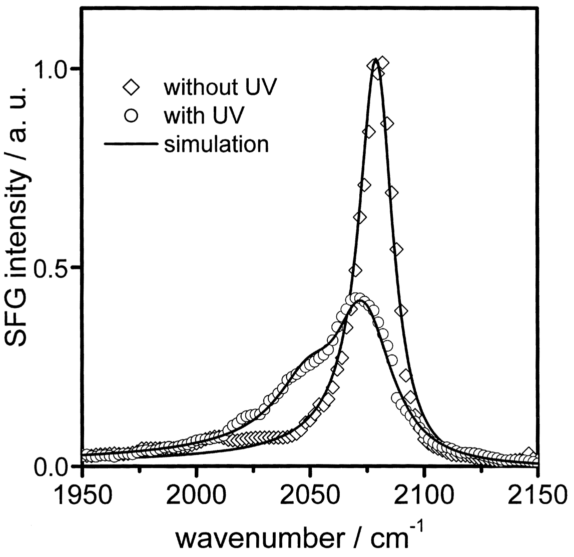

Fig. 5. Comparison of the theoretical and the experimental spectra. Circles and diamonds are the signal intensities observed under and without the UV pumping, respectively. Solid lines are calculated spectra. In the reproduction of the spectrum under the UV pumping, the anharmonicity constant $\omega_e x_e$ of 11.5 $\mathrm{cm^{-1}}$, the fractional population of 0.3 for the $v = 1$ level, and the broadening of the widths of the vibrational absorption band from 18 $\mathrm{cm^{-1}}$ to 31 $\mathrm{cm^{-1}}$ in FWHM for both the fundamental and hot band transitions were assumed. CPA was applied in the calculation with the parameters of $\tilde{U}$ (q) derived by $(\sqrt{7}/2 \times \sqrt{7}/2)R19.1°$ structure on Ni(111).

The value of the linear susceptibility was taken from the report by Campuzano and Greenler.[44] It is remarkable that no contribution of the 4WM signal is needed for the simultaneous reproduction of the spectra observed with and without the UV pumping. We also examined the lineshape with the populations at the $v = 2$ and higher levels to find that they should be much smaller by less than 1/10 than those of the $v = 0$ and 1 levels.

Let us now look at the UV-induced broadening, from 18 $\mathrm{cm^{-1}}$ to 31 $\mathrm{cm^{-1}}$. In our simulation, the same amount of the broadening for the $v = 1 \leftarrow 0$ and $v = 2 \leftarrow 1$ transitions has been assumed. The theory by Persson,[31] which is based on the excitation diffusion model, resulted in additional broadening parameters: the width for the $v = 1 \leftarrow 0$ transition increased but that for the $v = 2 \leftarrow 1$ transition decreased when the excited state population increased. The dispersion of the phonon band and the IR absorption intensity determine the magnitude of this width. The values of the parameters for the H-Si stretching vibration as given in the above paper are not so different from those used in the present calculation: the additional homogeneous width is estimated to be a few $\mathrm{cm^{-1}}$. Our claim that both the $v = 1 \leftarrow 0$ and $v = 2 \leftarrow 1$ transitions increased their widths by ~13 $\mathrm{cm^{-1}}$ may be acceptable.

Figure 6 shows the calculated SFG spectra for different ra-

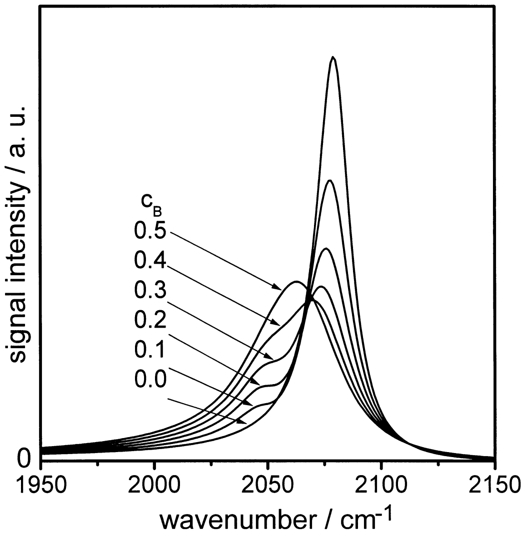

Fig. 6. The SFG spectra calculated for various fractional population ratios c_B of the $v = 1$ state.

tios of c_A (concentration of $v = 0$ CO):c_B (concentration of $v = 1$ CO). We assumed that the width increased in proportion to c_B from 18 cm^{-1} ($c_B = 0$) to 31 cm^{-1} ($c_B = 0.3$). In the calculation, the Fourier transform of the dipole interaction $\tilde{U}$ (q) was given by assuming the $(\sqrt{7}/2 \times \sqrt{7}/2)R19.1°$ structure of the CO/Ni(111) system with the image dipoles on an ideal metal surface. We put $\tilde{U}$ (0) = 0.088 Å^{-3}, $\alpha_e = 2.6$ Å^3, $\alpha_{vA} = 0.132$ Å^3 for "A" (1 Å = 0.1 nm), and $\alpha_{vB} = 2\alpha_{vA}$.[10,41]

C. Possibility of Vibrational Excitation by UV Pumping. We postulate the observed effect of the UV irradiation in the presently investigated CO/Ni(111) system to be as follows: that the adsorbed CO molecules are scattered by hot electrons/holes created by the UV pumping and undergo vibrational excitation and pure dephasing. The observed increase of the linewidth by ~13 cm^{-1} is ascribed to the overall dephasing. On the basis of the postulate, the efficiency of the vibrational excitation can be estimated as follows.

We derived from simulation that ~30% of the adsorbed molecules were excited to the $v = 1$ level by a single 150 μJ UV pulse. The number of photons absorbed at the Ni surface is estimated as 2×10^{13}/pulse from the reflectivity of light at 266 nm with 75° incident angle. The absorbed photon flux was then estimated as 1×10^{14} photons/pulse cm^2. When we assume each absorbed photon to generate one hot electron at the surface, the density of the generated hot electrons is ~10^{14} electrons/cm^2. As the irradiation of the UV pulse resulted predominantly in the vibrational excitation with negligible desorption, the occurrence number of the vibrational excitation events is about 2–3 per hot electron. Considering that photons penetrate to some depth and that only those hot electrons located at close vicinity of the surface interact with the adsorbed CO molecules, the number may be even larger.

There exist two models which may explain the highly efficient vibrational excitation: one postulating the promotion of hot electron to a negative ion state[45] and the other postulating the transformation of the energy of hot electrons into the energy of internuclear vibrations through non-adiabatic vibration/electron coupling.[46] Note that the internal excitation of CO molecule directly by the UV radiation of 4.3 eV is impossible since the highest occupied 5σ (and 1π) state is about 8 eV below the Fermi level.[47]

The scheme conceived by the first model is depicted in Fig. 7a. It was originally proposed to explain the photodesorption of NO from Pt in which the final transition brings the molecule to the continuum level of the ground state potential surface.[47–51] The surface state of the broad 2π* level (partially occupied due to back donation) is located at about 3.5 eV above the Fermi level,[52,53] and the UV-generated hot electrons are energetically capable of accessing the negative ion (Ni–CO$^-$) state. After the Franck–Condon transition to the ion state, the molecular state will propagate towards the potential minimum and will decay via another Franck–Condon transition back to the ground state, depositing the molecule in the excited vibrational state. In order to attain the high efficiency of vibrational excitation, each UV-generated electron has to scatter several times to generate the negative ion state before thermalization. We are not aware of a theory which deals with such multiple scattering process, and the needed model should also explain, under a proper consideration of the Franck–Condon factors and

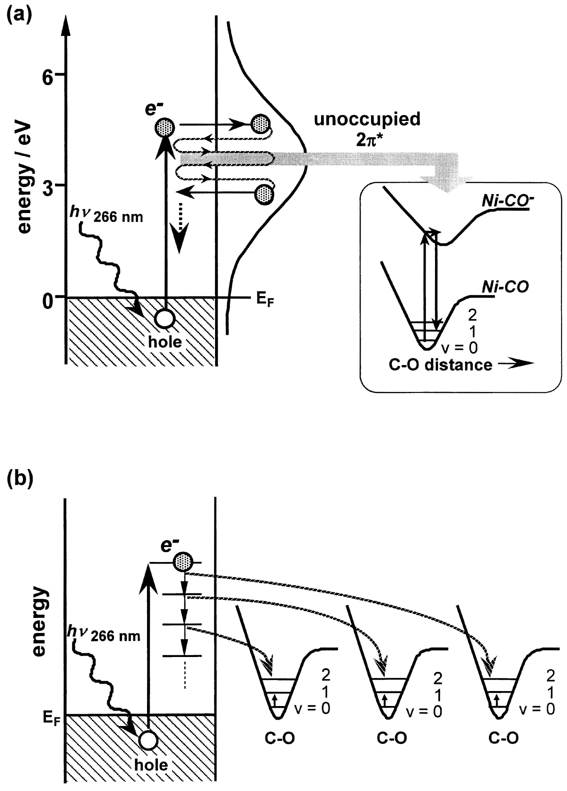

Fig. 7. Two conceivable schemes for the UV-induced transient vibrational excitation of adsorbed CO on Ni(111) surface. (a) Negative ion resonance model in which a photogenerated hot electron in the metal occupies the 2π* level leading to a temporary negative ion state. Inset illustrates the excitation of internal stretching mode of adsorbed CO by the scattering of the electron. (b) Non-adiabatic coupling model in which the photogenerated hot electron transfers its energy to the stretching mode of several CO molecules.

the dynamics of wave function in the associated potential curves, why the $v = 2$ and higher levels are not populated.

In applying the second model, which was proposed recently by Aizawa and Tsuneyuki[46] to explain the photodesorption of molecules from metals, we must include the stretching mode of adsorbed CO in the scheme of non-adiabatic coupling with a hot electron, as shown in Fig. 7b. The model may explain the high excitation efficiency when one conceives that several CO oscillators are involved in the interaction. However, we lack again the detailed knowledge of the magnitude of the coupling or the details of molecule-metal interaction and the electronic structure of the system.

Conclusion

The SFG spectrum was observed for the CO/Ni(111) system under the picosecond UV pumping, and the UV-induced changes, namely, the broadening of the vibrational band and the appearance of a new band, were found to take place during the pump period of 30 ps. The spectrum was reproduced by a simulation based on the dipole-dipole interaction with CPA scheme and on the hot band model. The features of the transient responses of both the fundamental and hot band signals indicated that the vibrational excitation is an electronically driven process; direct involvement of the hot electrons in the excitation of the CO internal stretching mode was feasible. A highly efficient excitation of the molecular vibration of the adsorbed CO was derived as an interpretation. Conceivable mechanisms for the process were described by postulating either the involvement of the intermediate negative ion resonance state or the occurrence of non-adiabatic coupling between hot electron and molecular vibration. We could not decide which is the physics of the process.

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