

# Measurement of low energy frustrated vibrational modes of CO on Ni(111) via inelastic electron scattering

Jeong Sook Ha and S.J. Sibener

*The Department of Chemistry and The James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637, USA*

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High-resolution electron energy loss spectroscopy (HREELS) has been used to study the low-energy vibrational modes of bridge-bonded CO on Ni(111) after a well-ordered  $c(4 \times 2)$  overlayer structure was formed. In this paper we report the spectroscopic observation of two low-energy modes of bridge-bonded CO on Ni(111) which have not been previously reported, as well as the momentum-resolved scattering for one of these modes. At  $T_s = 120$  K, under impact scattering conditions, a frustrated translation of CO parallel to the surface was observed at an energy loss of 11.8 meV. The dispersion curve measured along the  $\langle 11\bar{2} \rangle$  direction of Ni(111) for this mode was dispersionless, indicating that there is no direct lateral interaction between the adjacent CO molecules in this structure. At  $T_s = 170$  K, using a transient negative-ion  $\Sigma$  shape-resonance to enhance our sensitivity, a frustrated rotation for bridge-bonded CO was also observed at an energy loss of 37.5 meV. The energy of this mode is near the value previously estimated from temperature dependent infrared line shape measurements of the CO stretch peak position and lineshape, and is believed to be responsible for vibrational phase relaxation in the  $c(4 \times 2)$ -CO-Ni(111) system. The energies of the observed modes are also consistent with those derived from a simple cluster calculation.

## 1. Introduction

Precise information about the vibrational modes of molecules adsorbed at well characterized surfaces is essential for improving our understanding of molecular bonding at interfaces. Two primary techniques, infrared spectroscopy (IRS) and high-resolution electron energy loss spectroscopy (HREELS), have been used with much success to study the *high*-frequency vibrational modes of adsorbates for many systems. In contrast, very little is known about the *low*-frequency frustrated, i.e., hindered, translation and rotation modes for adsorbed molecules. This is unfortunate since these modes play a very important role in determining the dynamical behavior of adsorbed systems. These low-frequency modes are the first to become excited upon thermal excitation. Information on the energy and amplitude of these low-energy modes is important for understanding such fundamental processes as surface diffusion,

thermal desorption, and the vibrational dephasing of higher-lying excitations. Only recently has some information on these low-frequency modes been experimentally obtained [1–7]. Indirect information comes from a detailed temperature-dependent lineshape analysis of higher-lying vibrational modes, while direct information comes from actual spectroscopic observation of the low-frequency modes. Vibrational phase relaxation due to the anharmonic coupling of high-frequency vibrations with low-frequency ones (which has been inferred from temperature-dependent peak position and lineshape measurements) has been used to study the low-lying vibrations for several adsorbate/single-crystal systems: CO/Ni(111) [1], NO/Ru(001) [2], and NO/Ni(111) [3]. More direct measurements of the frustrated translations of CO on Pt(111) [4] and on Ni(100) [5] have been obtained using inelastic He atom scattering, while the frustrated translation and rotation of CO on Ni(110) [6] have been obtained using inelastic

electron scattering. Finally, the frustrated rotation of CO on Cu(100) has recently been seen with infrared reflection absorption spectroscopy (IR-RAS) in measurements made possible by a coupling of the normally forbidden transition for the frustrated rotation with an optically allowed infrared absorption band [7].

Bridge-bonded CO molecules have six nondegenerate normal modes: C–O internal stretch ( $\omega_1$ ), metal–CO stretch ( $\omega_2$ ), two “frustrated rotations” ( $\omega_3$ ,  $\omega_4$ ), and two “frustrated translations” ( $\omega_5$ ,  $\omega_6$ ) [8]. Richardson and Bradshaw [8] predicted that among these six modes only the frustrated translation which is perpendicular to the Ni–Ni bond axis ( $\omega_6 = 9$  meV) and the frustrated rotation with its plane of rotation parallel to the Ni–Ni bond axis ( $\omega_4 = 23$  meV) have resonance frequencies below the maximum Ni phonon frequency (37.6 meV). This prediction was based on a normal-mode analysis for CO adsorbed on a small Ni cluster. Other estimates come from temperature dependent line shape analysis of the C–O internal stretch, indirectly yielding a vibrational energy for the frustrated rotation of bridge-bonded CO as  $\omega_4 = 29$  meV [1].

In this paper we present the direct spectroscopic observation of the frustrated translation ( $\omega_6 = 11.8$  meV) of CO molecules on  $c(4 \times 2)$ -CO-Ni(111) at 120 K under impact scattering conditions. Momentum-resolved measurements involving this mode were also carried out, and revealed no dispersion along the  $\langle 112 \rangle$  direction of Ni(111). Such momentum-resolved measurements are particularly useful as they yield information on inter-adsorbate interactions. We also report that the frustrated rotation for bridge-bonded CO  $\omega_4$  occurs at an energy loss of 37.5 meV at  $T_s = 170$  K. This mode was obtained using a transient negative-ion  $\Sigma$  shape-resonance [9,10] to enhance our sensitivity.

## 2. Experiment

The experiments were performed on a Ni(111)  $\pm 0.2^\circ$  crystal surface, whose orientation was measured with Laue X-ray backreflection. The Ni(111) sample was cleaned and annealed by re-

peated cycles of Ar<sup>+</sup> ion sputtering and heating at 1173 K. Surface cleanliness and long-range order were checked by Auger spectroscopy ( $\theta_{\text{contaminant}} < 0.01$ ) and low-energy electron diffraction (LEED), respectively. The base pressure of the UHV-system was  $5 \times 10^{-11}$  Torr. The measurements on the frustrated translation and rotation modes were done at crystal temperatures of 120 and 170 K, respectively. The HREELS consists of a two-stage monochromator and a single-stage analyzer which are based on  $127^\circ$  cylindrical deflection optics [11,12]. The analyzer can be independently rotated in the scattering plane over a range of  $55^\circ$ , covering a total angle  $82^\circ < [\Theta_i + \Theta_f] < 137^\circ$ , where  $\Theta_i$  is the incident angle and  $\Theta_f$  is the outgoing angle with respect to the surface normal. The scattering plane includes the surface normal. The instrumental energy resolution was typically 5.0–5.5 meV, and the angular resolution was about  $1.5^\circ$ . Finally, the digital-to-analog converter which advanced the analyzer acceptance energy had a resolution of 0.3 meV/bit.

CO forms an ordered  $c(4 \times 2)$  overlayer structure at temperatures below 200 K when the CO coverage is  $\theta_{\text{CO}} = 0.5$ . During overlayer growth the CO molecules were dosed through a leak valve (uncalibrated ion gauge reading was  $1.3 \times 10^{-9}$  Torr) with  $T_s = 150$ – $170$  K. The actual extent of  $c(4 \times 2)$  growth was assessed by in situ monitoring of a half-order superlattice diffraction spot with the electron spectrometer’s angle-resolved analyzer. This diffraction spot was also used for aligning the azimuthal orientation of the crystal. Sharp  $c(4 \times 2)$  LEED spots were routinely observed with this growth procedure.

## 3. Results

It is well known [13–17] that all CO molecules occupy two-fold bridge sites in the  $c(4 \times 2)$  structure on Ni(111). In this experiment this was confirmed by the observation of a single internal stretch mode of C–O and a single metal–CO stretch. Fig. 1 shows such a spectrum for an ordered  $c(4 \times 2)$  CO layer on Ni(111) which was taken with a specular, i.e., dipole-allowed, scattering geometry. The observed energy loss peaks at

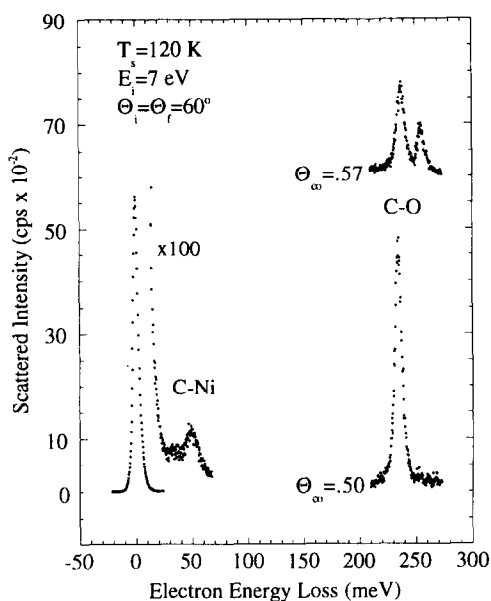


Fig. 1. Electron energy loss spectra of CO on Ni(111) at  $T_s = 120$  K. The lower spectrum is for a  $c(4 \times 2)$  overlayer, with  $\theta_{CO} = 0.50$ , and contains spectral features due to C–Ni and C–O stretch modes exclusively for bridge-bonded CO. The upper spectrum is for a CO saturated surface,  $\theta_{CO} = 0.57$ , and shows C–O stretch energies characteristic of both bridge and on-top bonded molecules. Experimental conditions: impact energy  $E_i = 7$  eV, incident angle  $\Theta_i = 60^\circ$  and outgoing angle  $\Theta_r = 60^\circ$ . Measurement times were 10 and 7 s/channel for the  $c(4 \times 2)$  and saturated overlayers, respectively.

49 and 234.5 meV are the characteristic metal–CO stretch and C–O internal stretch modes for bridge sites, respectively. (Measurements taken at very low exposure,  $\theta = 0.13$  L, had a C–O internal stretch of 224 meV, in agreement with the value seen with infrared spectroscopy [18,19] for three-fold site occupation.) The spectrum in fig. 2 was obtained using an off-specular impact scattering geometry along the  $\langle 11\bar{2} \rangle$  symmetry axis of Ni(111) with an impact energy of 190 eV. It shows the 11.8 meV loss and gain peaks which we assign to the frustrated translation,  $\omega_6$ , of CO moving from the two-fold bridge site towards the three-fold site on Ni(111). This assignment is based upon the previously reported normal mode and energy calculations for CO adsorbed on a Ni cluster [8]. Table 1 presents these calculated values along with our experimental findings. In order to make sure that this spectral feature was not from

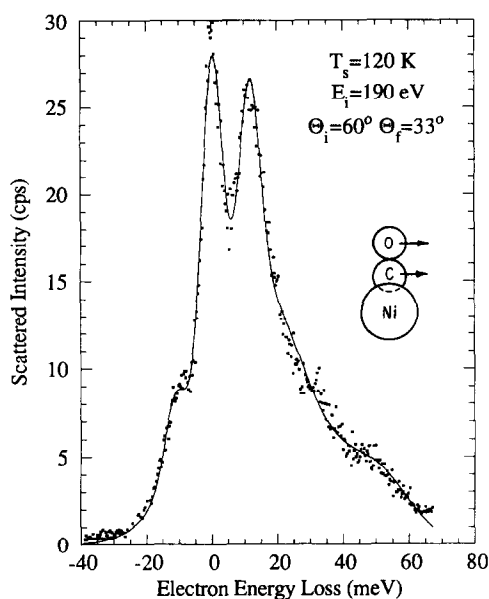


Fig. 2. Typical electron energy loss spectrum of  $c(4 \times 2)$ -CO-Ni(111) with impact energy  $E_i = 190$  eV. Inset figure shows the geometric displacements for the frustrated translation of bridge-bonded CO where molecular motion is perpendicular to the Ni–Ni bonding axis. The spectrum was collected along the  $\langle 11\bar{2} \rangle$  direction of Ni(111) with  $\Theta_i = 60^\circ$  and  $\Theta_r = 33^\circ$  and an accumulation time of 30 s/channel. The weak feature near 50 meV may be due to impact scattering excitation of the C–Ni stretch. The solid line is a nonlinear least-squares fit to the data which used Gaussian fitting functions.

the substrate's Rayleigh wave we measured its dispersion behavior along the  $\langle 11\bar{2} \rangle$  direction of Ni(111). The flat dispersion relation shown in fig. 3 clearly differs from the sinusoidal Rayleigh phonon mode of Ni(111) [12], and thus lends support

Table 1

Normal modes for bridge-bonded CO on Ni; theoretical values are from a relatively simple calculation for bridge-bonded CO on a six-atom Ni(100) cluster [8]

Normal mode	Energy (meV)		
	Cluster calc. [8]	Expt., this work	Mechanism
$\omega_1$	260.3	234.5	dipole
$\omega_2$	56.7	49.0	dipole
$\omega_3$	80.5	not observed	–
$\omega_4$	22.8	37.5	resonance
$\omega_5$	70.9	not observed	–
$\omega_6$	9.4	11.8	impact

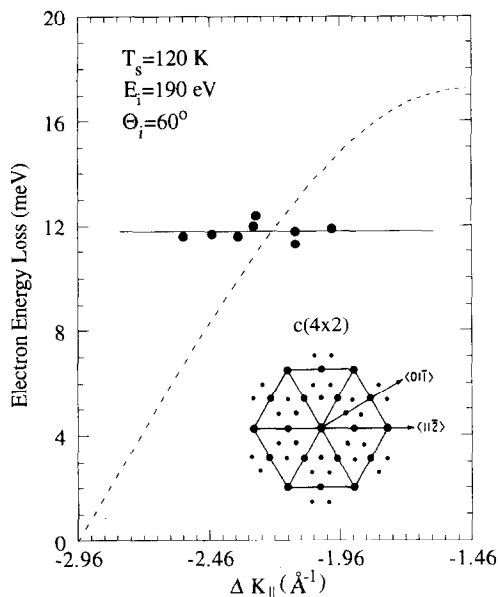


Fig. 3. Dispersion curve measured for the frustrated translation of CO (11.8 meV) along the  $\langle 11\bar{2} \rangle$  direction of Ni(111) for  $c(4 \times 2)$ -CO-Ni(111) at  $T_s = 120$  K. Inset figure shows a schematic LEED pattern for three superimposed orientational domains of  $c(4 \times 2)$  symmetry. The dotted line is the dispersion curve for the Rayleigh wave on clean Ni(111) [12]. Experimental conditions: impact energy  $E_i = 190$  eV and incident angle  $\Theta_i = 60^\circ$ .

to our spectroscopic assignment. No evidence was seen in fig. 3 for an avoided crossing which involved these two surface vibrational modes. This may be due to weak coupling and/or limited energy and angular resolution. Signals were not collected near the  $(\frac{1}{2}, \frac{1}{2})$  and  $(\bar{1}, \bar{1})$  diffraction peaks due to interference from the large diffuse elastic intensity in these regions. We also note that the inelastic signal arising from the frustrated translational mode was always stronger (by a factor of two or so) as the outgoing angle was moved closer to the surface normal, i.e., the intensity measured between the  $(\frac{1}{2}, \frac{1}{2})$  and  $(\bar{1}, \bar{1})$  diffraction peaks was stronger than that between the  $(0, 0)$  and  $(\frac{1}{2}, \frac{1}{2})$  ones. Most measurements reported in this paper were done using such a geometry. (The same trend was observed in our earlier studies of phonon excitation on clean Ni(111) [12].) Finally, we also explored the inelastic intensity arising from different incident scattering conditions since parameters such as electron energy and scattering

geometry can influence excitation probabilities [20]. Measurements employing impact energies between 110 and 240 eV were taken with the analyzer set to collect signal at the same parallel momentum transfer,  $\Delta K_{\parallel} = -2.35 \text{ \AA}^{-1}$ . This was done by varying the analyzer angle while maintaining the incident angle at  $\Theta_i = 60^\circ$ . The peak intensity of the energy loss feature arising from the frustrated translation was approximately constant in this range,  $I = 22\text{--}29$  cps.

The frustrated translation should be sensitive to adsorbate-adsorbate interactions within the compressed CO layer. This mode is polarized parallel to the surface and the mutual CO distances (charge density overlap) change during the vibration. The data shown in fig. 3 indicate that the energy of the frustrated translation (11.8 meV) was independent of parallel momentum transfer  $\Delta K_{\parallel}$ , suggesting that interactions between adjacent CO molecules are negligible in this  $c(4 \times 2)$  overlayer. This overlayer has a mutual CO distance of  $3.3 \text{ \AA}$  [17]. A similar lack of measurable dispersion was seen for  $c(4 \times 2)$ -CO-Pt(111) [4] in which the CO-CO distance is  $3.67 \text{ \AA}$ . Contrasting the behavior found for these two systems is the case of the  $(2 \times 1)$ -CO-Ni(110) [6] which has a mutual CO distance of  $3.05 \text{ \AA}$ . Here repulsive inter-adsorbate interactions resulted in significant dispersion. The above trend seems reasonable when we note that the van der Waals radius of oxygen is  $1.4 \text{ \AA}$  [21].

We now turn our attention to the frustrated rotation mode for bridge-bonded CO. Fig. 4 shows an electron energy loss spectrum for the  $c(4 \times 2)$  overlayer taken under experimental conditions which were chosen to enhance the vibrational excitations of CO on Ni(111) via a  $\Sigma$  shape-resonance at  $E_i = 18$  eV [9,10]. Such enhancement can occur when the equilibrium geometry of the transiently formed negative-ion differs from that of the initially neutral molecule-surface system [22]. Angle and energy dependent measurements will be reported elsewhere which explored in detail the nature of this resonance [10]. (The loss peak at  $37.5$  meV showed an impact energy dependence peaking at  $E_i = 18$  eV within the range  $7\text{--}30$  eV.) To summarize our findings, only the usual Ni-CO stretch mode at  $49$  meV was observed under specular scattering conditions with  $\Theta_i = \Theta_r = 65^\circ$  and

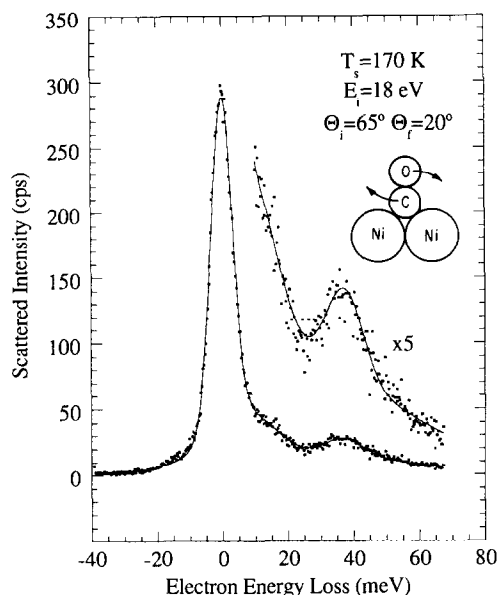


Fig. 4. Electron energy loss spectrum of a frustrated rotation of CO (37.5 meV) on  $c(4 \times 2)$ -CO-Ni(111) at  $T_s = 170$  K. Inset figure shows the geometric displacements for the frustrated rotation of bridge-bonded CO, which for this mode is parallel to the Ni–Ni bonding axis. Experimental conditions: impact energy  $E_i = 18$  eV, incident angle  $\Theta_i = 65^\circ$  and outgoing angle  $\Theta_f = 20^\circ$  along the  $\langle 11\bar{2} \rangle$  direction of Ni(111). Spectral accumulation time: 5 s/channel. The solid line is a nonlinear least-squares fit to the data which used Gaussian fitting functions.

$E_i = 18$  eV. However, as the outgoing angle was moved away from the specular geometry, i.e., toward the surface normal, a new energy loss peak at 37.5 meV appeared with intensity monotonically increasing as the surface normal was approached. This behavior was expected for coupling via this type of shape-resonance since the angular profile of the relevant CO molecular orbital peaks along the CO internuclear axis. Measurements on clean Ni(111) were performed under the same scattering conditions as described above in order to confirm that the observed energy loss peak was not due to a substrate phonon. The 37.5 meV loss peak was completely absent on the clean surface. Examination of the six vibrations predicted from the normal mode analysis of CO on a small Ni cluster [8], table 1, allows us to assign this excitation as a frustrated rotation,  $\omega_4$ , which is parallel to the Ni–Ni bonding axis. We also note that the experimentally observed peak is near

the value previously estimated for  $\omega_4$  based upon temperature dependent infrared line shape measurements of the CO stretch peak position and lineshape [1]. Such measurements have indicated that this particular frustrated rotation is most likely responsible for vibrational phase relaxation in the  $c(4 \times 2)$ -CO-Ni(111) system [1].

To complete this study we also attempted a series of isotopic substitution experiments with  $^{13}\text{CO}$  and  $^{12}\text{CO}$ . The C–O internal stretch for bridge-bonded CO in the  $c(4 \times 2)$  overlayer showed the expected red shift upon replacement of  $^{12}\text{CO}$  by  $^{13}\text{CO}$ , moving from 234.5 to 230.8 meV at  $T_s = 110$  K, respectively. Insufficient resolution of the spectrometer prohibited observation of an isotope shift for the low-frequency CO frustrated translation. The frustrated rotation for bridge-bonded CO did not, within our resolution, show any isotope effect either. In addition to resolution limitations, this result might not be surprising since the energy of the frustrated rotation for bridge-bonded CO is close to the maximum surface phonon frequency (37.6 meV) of Ni(111). Mode hybridization seems likely in this nearly degenerate situation.

Finally, we decided to grow a CO-saturated  $(\sqrt{7}/2 \times \sqrt{7}/2)$ -R19.1° structure with  $\theta_{\text{CO}} = 0.57$  [15,17] in order to see if an isotopic shift could be seen for this overlayer. We observed the LEED pattern for this structure, although the diffraction spots were not as sharp as those for the  $c(4 \times 2)$  overlayer. This compressional overlayer has a 3 : 1 ratio of bridge-bonded to on-top bonded CO molecules [17]. (Note that the simple cluster calculation of Richardson and Bradshaw [8] gives 51 meV for the frustrated rotation of on-top bonded CO as compared to 23 meV for the bridge site.) Electron energy loss measurements gave a clear and reproducible (three comparative measurements were performed) red shift for  $^{13}\text{CO}$  (43 meV) with respect to  $^{12}\text{CO}$  (45.4 meV) on this overlayer. This is shown in fig. 5. The presence of this shift confirms that this spectral feature is due to CO and is not due to a surface phonon excitation of the Ni substrate. The observed shift most likely arises from the occupation of on-top sites in the  $(\sqrt{7}/2 \times \sqrt{7}/2)$ -R19.1° structure. We say this since the spectral shift due to changing adsorbate

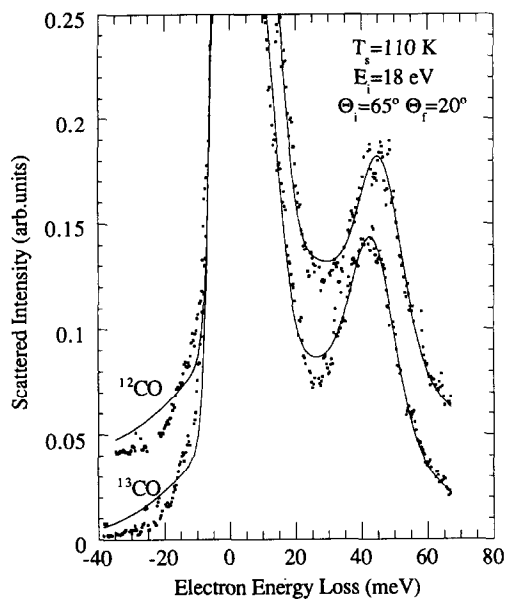


Fig. 5. Spectral shift due to isotopic substitution of the frustrated rotation mode for saturated CO coverage on Ni(111). The upper spectrum is for the saturated  $^{12}\text{CO}$  overlayer while the lower one is for  $^{13}\text{CO}$ . Experimental conditions:  $T_s = 110$  K,  $E_i = 18$  eV,  $\theta_i = 65^\circ$  and  $\theta_f = 20^\circ$ . The  $^{12}\text{CO}$  and  $^{13}\text{CO}$  spectra were averaged for 4.5 and 10 s/channel, respectively. The solid line is a nonlinear least-squares fit to the data which used Gaussian fitting functions.

mass is expected to be greater for on-top bonded CO than for bridge-bonded ones due to a larger effective mass change upon isotopic substitution. The red shift due to  $^{13}\text{CO}$  adsorption is comparable with recent (higher resolution) infrared reflection absorption studies of the CO frustrated rotational mode on Cu(100) [7]. In this study on-top bonded CO–Cu(100) showed a frequency shift of  $\sim 1.5$  meV upon  $^{13}\text{C}$  substitution.

#### 4. Conclusions

In this paper we have reported the spectroscopic observation of two previously unseen low-energy vibrational modes for bridge-bonded CO arranged in a  $c(4 \times 2)$  structure on Ni(111). These are the frustrated translation,  $\omega_6$ , located at 11.8 meV at  $T_s = 120$  K, and the frustrated rotation,  $\omega_4$ , located at 37.5 meV at  $T_s = 170$  K. In addition to these measurements we also studied the disper-

sion curve for the frustrated translation mode along the  $\langle 11\bar{2} \rangle$  symmetry direction of Ni(111) and found it to be dispersionless, indicating that there is no significant lateral interaction between adjacent CO molecules in this structure. These measurements will be useful for improving our understanding of chemical bonding, vibrational dephasing, surface diffusion, and desorption processes for this well defined adsorption system.

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