

Interadsorbate interactions in the $c(4\times 2)$ NO/Ni(111) system

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Electron energy loss spectroscopy has been used to map the dispersion of the dipole active internal NO stretch and of the NO frustrated translation, which has not been previously observed, in the $c(4\times 2)$ NO/Ni(111) system. The dispersion of the dipole active mode was fit with a model that assumed electrostatic dipole–dipole coupling (including image dipoles) between the adsorbates. The frustrated translation, on the other hand, showed no dispersion to within the resolution of the experiment across the entire surface Brillouin zone of the Ni(111) substrate. These measurements reveal new information on interadsorbate interactions in an important model system. © 1995 American Institute of Physics.

I. INTRODUCTION

The formation of ordered overlayers of adsorbates implies the existence of interadsorbate interactions. These interadsorbate interactions have attracted a great deal of study over the past 20 years, in attempts to gain some insight into the nature of the surface chemical bond. As an example, comparison of the differing adsorption geometries of NO on Pt(111), Pd(111), and Ni(111) shows that while NO forms a high coverage 0.5 ML ordered $c(4\times 2)$ structure on Ni(111) at room temperature, on the Pt(111) surface NO adsorbs in a disordered fashion above 0.25 ML,¹ and on Pd(111) it also forms a 0.5 ML $c(4\times 2)$ structure, but can go on to form a higher coverage 0.75 ML (2×2) structure.^{2,3} Studies such as these have underlined the need for further research on the intermolecular interactions in these systems, and have served as partial motivation for this work.

The NO/Ni(111) system has been investigated for many years using a wide variety of surface science techniques, including ultraviolet photoemission spectroscopy (UPS),^{4–6} angle resolved UPS (ARUPS),⁷ x-ray photoemission spectroscopy (XPS),⁵ low energy electron diffraction (LEED),^{5–8} electron stimulated desorption ion angular distribution (ESDIAD),⁸ high resolution electron energy loss spectroscopy (HREELS),⁹ and infrared absorption spectroscopy (IRAS).^{10,11} NO is known to adsorb molecularly on Ni(111) below 300 K, giving a $c(4\times 2)$ LEED pattern near 0.5 ML coverage. The HREELS and IRAS studies of this system have shown two distinct NO stretching frequencies at low coverages, and a single stretching frequency at coverages near 0.5 ML. Formerly, these two bands were assigned to NO adsorbed at bridge sites in a bent geometry at low coverages, and to an upright geometry at high coverages. Recently, photoelectron diffraction (PED),¹² surface extended x-ray absorption fine structure (SEXAFS),¹³ and LEED I–V analysis^{1,14} have been used to show that the local adsorption site of the NO molecule is a threefold hollow site, contradicting the earlier assignments based on vibrational frequencies alone. Using symmetry arguments in addition to dynamical LEED analysis, Mapledoram *et al.*¹⁴ have shown that the NO molecule is adsorbed in both fcc and hcp threefold hollow sites on Ni(111) at all coverages, and Materer *et al.*¹ have suggested that the two distinct stretching frequencies observed in the HREELS and IRAS spectra are in

fact due to dipole–dipole coupling between NO molecules with and without nearest neighbors in the 0.5 ML structure (Fig. 1), and not to a change in local adsorption geometry with coverage as was previously believed. Other studies, particularly of CO on transition metal and noble metal surfaces, have shown that the frequency shift of the internal stretch vs increasing coverage in these systems is usually a combination of an upward shift due to dipole coupling, and a static chemical shift which may either increase or decrease the total frequency shift, depending on its sign.¹⁵

In the present work we report the first observation of a new adsorbate mode for this system, the frustrated (i.e., hindered) translation of the NO molecule parallel to the surface, and discuss the fact that this mode does not disperse in the context of the lateral interactions between NO molecules in the compressed NO overlayer. We present evidence that the frequencies of these modes may be a good indication of the local adsorption geometry. Also, we present a study of the dispersion of the dipole active NO intramolecular stretch along two high symmetry directions of the Ni(111) lattice for both the ordered $c(4\times 2)$ 0.5 ML structure and a structure of about 0.4 ML, which also exhibits a $c(4\times 2)$ LEED pattern. The dispersion curve of the NO stretch was fit with a model that assumed dipole–dipole coupling between molecules in the adsorbate overlayer. In addition, we demonstrate that such dispersion curves are an alternate source of information on the magnitudes of the frequency shifts due to dynamic dipole coupling and static chemical effects.

II. EXPERIMENT

The experiments were carried out in a two level UHV chamber that has been described previously.¹⁶ Briefly, the chamber, pumped by a 300 l s⁻¹ ion pump and with base pressure less than 1×10^{-10} Torr, is equipped with a HREELS spectrometer, an ion gun, an Auger spectrometer, and LEED optics. It also includes a threefold differentially pumped supersonic molecular beam source which strikes the target at the focus of the HREELS optics. The flux of the molecular beam was calibrated using an in-line apertured ion gauge flux meter. The Ni crystal could be cooled to 115 K with liquid nitrogen and heated to 1200 K by electron bombardment of the back of the crystal. Temperatures were measured with a type K thermocouple which was spot welded to

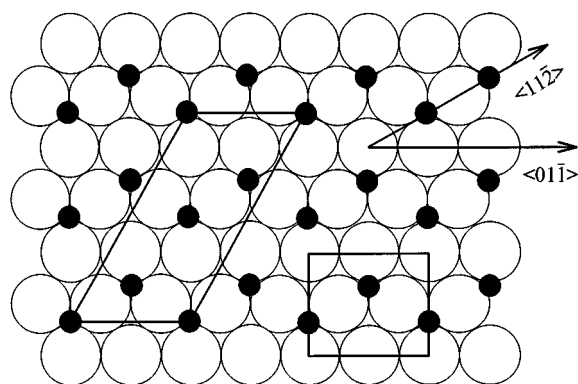


FIG. 1. Model of the 0.5 ML overlayer of NO on Ni(111) as determined by Mapledoram *et al.* (Ref. 14) that leads to the $c(4 \times 2)$ LEED pattern. The NO molecules are adsorbed in both fcc and hcp threefold hollow sites. A $c(4 \times 2)$ unit cell, a primitive unit cell, and the experimental scattering directions are outlined for clarity.

the side of the crystal. The crystal surface was cleaned by repeated cycles of Ar^+ ion sputtering, followed by annealing at 1100 K; surface cleanliness was verified by both Auger and HREELS spectroscopies.

The ordered NO overlayers were prepared by dosing at a surface temperature of 120 K, by either dosing the clean surface with the molecular beam or by backfilling of the chamber, followed by annealing at 270 K for 2 min.^{11,14} The experiments were carried out at two coverages, one near 0.4 ML, and one corresponding to the 0.5 ML $c(4 \times 2)$ overlayer shown in Fig. 1. The 0.5 ML overlayer was prepared by either several dose and anneal cycles with the molecular beam until the NO stretch frequency as monitored with HREELS reached a maximum of 196 meV and remained unchanged with further dosing, or by overexposing the crystal with background dosing followed by annealing at 270 K. Sharp $c(4 \times 2)$ LEED patterns were routinely achieved with both of these dosing methods. The 0.4 ML overlayer was prepared by dosing with the calibrated molecular beam to an exposure of approximately $8 \times 10^{14} \text{ cm}^{-2}$, a coverage that is characterized by an internal NO stretch frequency of about 193.5 meV. After the overlayers were annealed at 270 K, a sharp $c(4 \times 2)$ LEED pattern appeared. The LEED pattern of the 0.4 ML overlayer was indistinguishable to the eye from the LEED pattern of the full 0.5 ML overlayer. Figure 2 shows a specular HREELS spectrum of the 0.5 ML $c(4 \times 2)$ overlayer, which shows two dipole allowed bands. The higher energy band at 196 meV is due to the NO intramolecular stretch and the weak loss at about 45 meV is due to the Ni–NO stretch, i.e., the NO hindered translation perpendicular to the surface. No differences were detected in the HREELS spectra or the LEED patterns of the 0.5 ML overlayers prepared by background dosing or molecular beam dosing.

III. RESULTS

A. NO frustrated translation

Figure 3 shows two HREELS spectra taken with off-

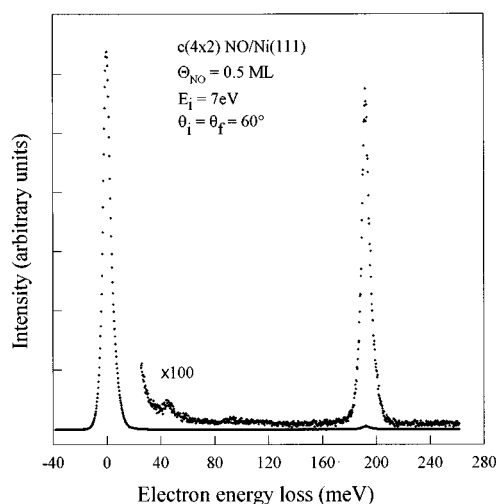


FIG. 2. Dipole scattering spectrum of the 0.5 ML overlayer of NO on Ni(111), showing the NO internal stretch at 196 meV and the NO–metal stretch at about 45 meV.

specular geometry in the high energy impact scattering regime: one for a clean Ni(111) surface and the other after adsorption of a 0.5 ML $c(4 \times 2)$ overlayer of NO. The spectra were taken along the $\langle 01\bar{1} \rangle$ direction of the Ni substrate under identical kinematic scattering conditions. The solid lines are nonlinear least squares fits to the data which used Lorentzian fitting functions. We assign the loss at approximately 11 meV to a frustrated translation of the NO molecule parallel to the surface, based on several criteria. Previous infrared line shape studies of this system had estimated the energy of the NO frustrated translation to be about 7.5 meV from the temperature dependence of the vibrational line shape of the

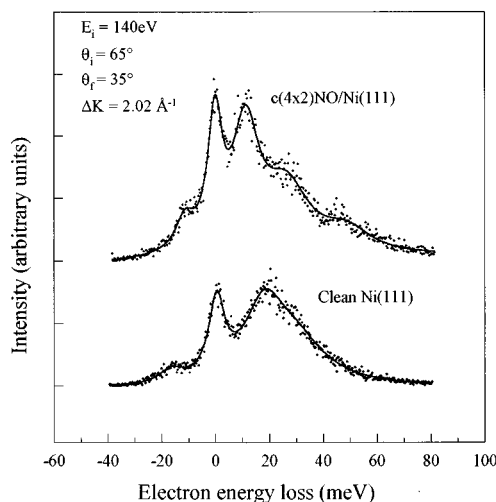


FIG. 3. Impact scattering spectra of the clean Ni(111) surface and of the Ni(111) surface after adsorption of a $c(4 \times 2)$ overlayer of NO, taken under identical scattering conditions. The loss at ca. ± 11 meV in the spectrum of the NO covered surface has been assigned to the frustrated translation of the NO parallel to the surface. The broad loss at ca. 20 meV in the spectrum of the clean surface is due to a surface resonance of the bulk phonon bands.

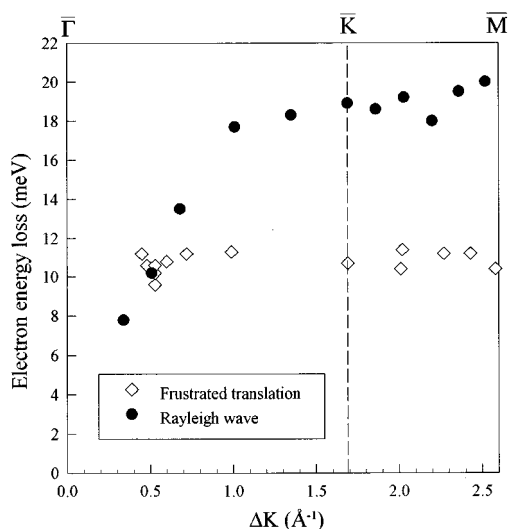


FIG. 4. Experimentally determined dispersion curves for the NO frustrated translation in the $c(4\times 2)$ overlayer on Ni(111). Also shown is the dispersion of the Rayleigh wave of clean Ni(111). The spectra were taken along the $\langle 01\bar{1} \rangle$ direction of the Ni(111) substrate. The dotted line at 1.69 \AA^{-1} is the edge of the substrate surface Brillouin zone at \bar{K} .

NO internal stretch,¹¹ where line broadening of the high energy mode was attributed to anharmonic coupling to the lower energy frustrated translation. We also note that the energy of this feature is similar to that calculated using cluster calculations for the frustrated translation of another diatomic molecule, CO,¹⁷ as well as to a feature assigned to frustrated translations of CO adsorbed in threefold sites in the $c(4\times 2)$ structure on Ni(111)¹⁸ [CO on Ni(111) is now known to adsorb in threefold hollow sites¹⁹]. This feature is absent on the clean surface, and the energy of this feature at the substrate Brillouin zone edge is well below that of the Rayleigh wave and bulk phonon bands of Ni(111), thus precluding its assignment as a substrate mode.

Figure 4 shows the dispersion of the frustrated translation along the $\langle 01\bar{1} \rangle$ symmetry direction of the Ni substrate, as well as the experimentally determined dispersion of the Rayleigh wave of the clean Ni surface in this direction. The energy and dispersion behavior of the frustrated translation were the same along other symmetry directions and for the 0.4 ML coverage. We would like to note that because the intensity of the losses due to the frustrated translation and the Rayleigh wave depend nontrivially on the scattering geometry and incident electron energy,¹⁶ it was necessary to determine empirically the differing conditions to best resolve the two features. To within 1 meV, the frustrated translation was dispersionless across the entire Brillouin zone of the Ni substrate.

B. NO intramolecular stretch

Figure 5 shows the HREELS spectra of the dipole active NO intramolecular stretching vibration in the 0.5 ML overlayer for a series of progressively larger parallel momentum transfers. Figures 6(a) and 6(b) show the dispersion of this mode as a function of \mathbf{K} along the $\langle 11\bar{2} \rangle$ ($\bar{\Gamma}-\bar{M}$) and $\langle 01\bar{1} \rangle$

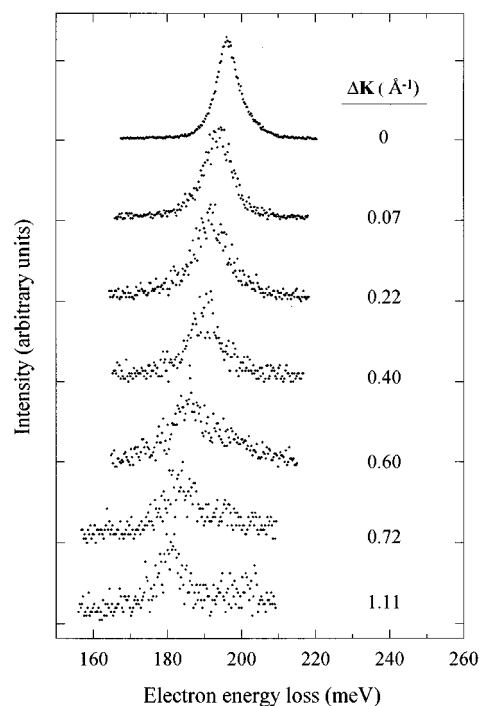


FIG. 5. Representative HREELS spectra showing the dispersion of the dipole active NO intramolecular stretch in the 0.5 ML overlayer for a series of progressively larger $\Delta\mathbf{K}$. The spectra were taken with incident energies from 7 to 18 eV and a variety of incident and final angles in order to reach the desired parallel momentum transfers.

($\bar{\Gamma}-\bar{K}$) directions of the Ni substrate for the 0.4 and 0.5 ML coverages, respectively. The solid lines are fits to the data using a model of electrostatic dipole-dipole coupling first proposed in Ref. 20, and modified as in Ref. 21 to include the effect of image dipoles. In this model, the frequency shift as a function of the momentum transfer parallel to the surface (\mathbf{K}) is given by

$$\frac{\omega^2(\mathbf{K})}{\omega_0^2} = 1 + \frac{\alpha_v \Sigma(\mathbf{K})}{1 + \alpha_e \Sigma(\mathbf{K})}, \quad (1)$$

where ω_0 is known as the singleton frequency, the frequency of the NO molecular stretch perturbed by the same static chemical environment as in an adsorbed overlayer, but without the effect of dipole coupling. α_e and α_v are the electronic and vibrational polarizabilities, respectively. $\Sigma(\mathbf{K})$ is known as the dipole sum, and is given by

$$\Sigma(\mathbf{K}) = \sum_l' \exp(i\mathbf{K}\cdot\mathbf{r}_l) \left(\frac{1}{|\mathbf{r}_l|^3} + \frac{1}{|\mathbf{r}_l + \mathbf{D}_l|^3} - \frac{3\mathbf{D}_l^2}{|\mathbf{r}_l + \mathbf{D}_l|^5} \right), \quad (2)$$

where the prime indicates that the infinite self-interaction term is omitted. The sum runs over the molecules in the real space lattice, and the last two terms are the contributions to the dipole sum due to the image dipole at a position given by $\mathbf{D}=(0,0,-2d)$, where d is the height of the dipole above the surface. The calculation was somewhat sensitive to the parameter d , which was varied between 1.92 \AA (i.e., the height of the center of the NO bond above the surface¹) and 1.0 \AA .

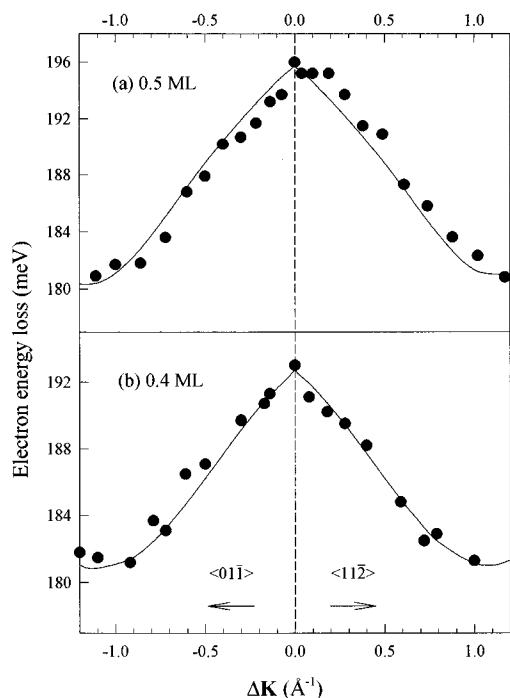


FIG. 6. The dispersion of the dipole active NO internal stretch along the two high symmetry directions of the Ni(111) substrate for the 0.5 ML $c(4 \times 2)$ overlayer (a), and the 0.4 ML overlayer (b). The solid lines are the fits to the data using the dipole-dipole coupling model as explained in the text.

The dipole sums were calculated for a single domain of the 0.5 ML structure, consisting of two superimposed sublattices of 100×100 dipoles. Each of these sublattices corresponds to one of the two superimposed 0.25 ML $c(4 \times 2)$ lattices, one of which is outlined in Fig. 1. In both the $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ directions, the NO stretch of the 0.5 ML overlayer disperses downward by 15 meV, or about 8% with respect to its value at the center of the surface Brillouin zone. Equally good fits were obtained by using dipole sums calculated with $d = 1.0 \text{ \AA}$ or with $d = 1.92 \text{ \AA}$. The parameters obtained from fitting the calculation to the 0.5 ML data were $\omega_0 = 185.9 \text{ meV}$, while α_e and α_v were 5.9 and 0.92 \AA^3 , respectively, for $d = 1.0 \text{ \AA}$, and α_e and α_v were 8.0 and 1.24 \AA^3 , respectively, for $d = 1.92 \text{ \AA}$. The 0.4 ML data were fit with two dipole sums that made different assumptions about how adsorption sites were filled. The first case assumed statistical occupation of the $c(4 \times 2)$ overlayer sites, obtained by multiplying the dipole sum $\Sigma(\mathbf{K})$ by a factor of 0.8,²⁰ and the second used dipole sums that simulated the presence of islands of local 0.5 ML coverage. Because of the rapid $1/r^3$ convergence of the dipole sum, the dipole sum for islands larger than about ten molecules on a side was essentially the same as for the full 0.5 ML overlayer. While the polarizabilities varied when fitting the 0.4 ML data with either model, the singleton frequency ω_0 remained the same at 184.2 meV.

IV. DISCUSSION

A. NO frustrated translation

We have investigated the intermolecular interactions of NO adsorbed on the Ni(111) surface through measurements

of the dispersion of two adsorbate vibrational modes. Because these two modes are polarized in mutually perpendicular directions (to first order), their dispersion behavior yields information on two physically quite different types of coupling. The frustrated translation, polarized parallel to the surface, is usually thought to be coupled to other adsorbate molecules through either direct Pauli repulsion of overlapping molecular orbitals, or through longer ranged repulsive static dipole-dipole coupling.²² On the other hand, the NO internal stretch does not change the intermolecular distance between adsorbates, and dispersion in this case is usually attributed to dynamic dipole-dipole coupling. Pauli repulsion is essentially only a nearest neighbor effect, while the $1/r^3$ dependence of dipole-dipole coupling makes this interaction quite long ranged. The dispersion or lack of dispersion of these two modes furnishes valuable information on these two types of coupling, and the energies of the perpendicular and parallel hindered translations can lend insight into the shape of the molecule-surface potential surface.

The dispersionless behavior of the NO frustrated translation is characteristic of most of the frustrated translations observed so far, despite the relatively small nearest neighbor distance of NO in the $c(4 \times 2)$ overlayer, 2.87 \AA . Frustrated translations of CO have now been observed experimentally for a number of substrates, and it has been found that these modes are almost all dispersionless. Of the substrates so far studied; Ni(111),¹⁸ Ni(100),²³ Ni(110),²¹ Pt(111),²⁴ Ir(100),²⁵ Fe(110),²⁶ and Rh(111),²⁷ only two have shown dispersion of the CO frustrated translation; CO/Ni(110) and CO/Rh(111). To our knowledge this is the first observation of a frustrated translation of NO on any surface. Dispersion of modes polarized parallel to the surface is sometimes attributed to direct Pauli repulsion of overlapping molecular orbitals. The van der Waals radii of nitrogen and oxygen in the gas phase are about 1.5 \AA ,²⁸ which is somewhat larger than half the nearest neighbor distance here. The displacement involved in the vibration of this mode can be used as an estimate of the degree of orbital overlap expected. In the harmonic approximation as described by Cyvin,²⁹ the mean amplitude of the frustrated translation at 120 K is about 0.11 \AA . The lack of dispersion of the frustrated translation of NO on this surface should be contrasted to the dispersion of CO on the Ni(110) surface. This system, with a nearest neighbor CO distance of 3.05 \AA , showed a dispersion of almost 50% at the adsorbate surface Brillouin zone edge with respect to the energy at the zone center, in both the high symmetry directions measured.²¹ The other system that has demonstrated dispersion, CO/Rh(111), showed a much more modest frequency shift of about 7% at the zone edge with respect to its value at the zone center. With our HREELS spectrometer, we should be able to detect a frequency shift of $\pm 1 \text{ meV}$, or about 10% of the value of the vibration at the zone center. It is quite possible that the intermolecular coupling of this mode is small enough to lead to dispersion less than this limit. However, as seen above, most other frustrated translations have also been shown to be dispersionless, both with HREELS and with helium atom scattering, which has significantly better resolution than HREELS. The extreme dispersion of the

frustrated translation in the CO/Ni(110) system appears to be unique among those systems studied so far.

The energies of most of the CO frustrated translations so far observed, 4–7 meV, are in general significantly lower than the energy of the NO frustrated translation that we observe, 11 meV. A notable exception is the energy of the frustrated translation of CO on the Ni(111) surface, 12 meV.¹⁸ NO¹ and CO¹⁹ adsorb in identical structures on the Ni(111) surface, both occupying threefold hollow adsorption sites. In contrast, the local adsorption site of CO on all the remaining surfaces is thought to be either an atop site or a combination of atop and bridge sites. The frequencies of the frustrated translations parallel to the surface thus may serve as a more reliable indication of local adsorption geometry than the frequencies of intramolecular stretching vibrations, which have recently been shown to result in inaccurate assignments for both CO/Ni(111)¹⁹ and NO/Ni(111).^{1,14}

B. NO intramolecular stretch

The NO internal stretch exhibited strong dispersion of 12 meV (6%) in the 0.4 ML overlayer and 15 meV (8%) in the 0.5 ML overlayer. Both of the dispersion curves could be fit with a model that assumes only dipole–dipole coupling between the adsorbates, but there were added difficulties with this system due to the presence of three orientationally distinct domains, and a glide plane in the adsorbate unit cell. The presence of a glide plane demands that there be more than one molecule in the adsorbate unit cell, which in this case effectively doubles the size of the adsorbate surface Brillouin zone along the $\langle 01\bar{1} \rangle$ direction.^{21,30} In the $\langle 11\bar{2} \rangle$ direction, two NO stretch modes should be observable, corresponding to the symmetric and antisymmetric (observable only off specular) combinations of NO molecular vibrations in the unit cell.²¹ However, this splitting of the NO stretch vibration along $\langle 11\bar{2} \rangle$ was not observed in this experiment under any of the scattering conditions we used. We attribute this to the observed spectrum being a superposition of (instrumentally broadened) spectral features due to multiple adsorbate domains, which result from the combination of a rectangular adsorbate lattice and a hexagonal substrate lattice. This means that the scattering direction in the adsorbate Brillouin zone is not well defined. For example, scattering along the $\langle 11\bar{2} \rangle$ direction of the Ni(111) lattice results in scattering along the high symmetry $(\bar{\Gamma}-\bar{Y})$ direction of the adsorbate surface Brillouin zone in only one domain, with the other two domains contributing scattering *across* the Brillouin zone of the adsorbate. This could obscure features that one would expect to observe when scattering in high symmetry directions of the adsorbate lattice, such as the splitting of the symmetric and antisymmetric combinations of the NO stretch.

In light of this complication, the dipole sums were calculated independently for the three domains, one with the scattering vector in the high symmetry direction and two (mutually equivalent) with the scattering vector oriented across the adsorbate Brillouin zone. Figure 7 shows the calculated dipole sums for the directions in the adsorbate Brillouin zone (inset) that result from scattering along the $\langle 11\bar{2} \rangle$ direction of the Ni(111) substrate. This figure shows that the

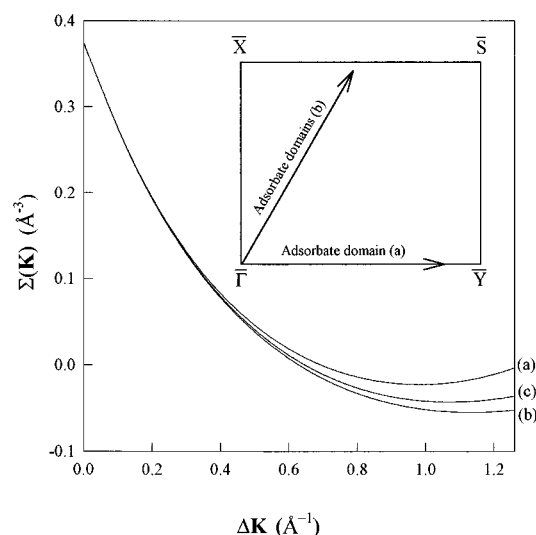


FIG. 7. The calculated dipole sums as a function of \mathbf{K} for scattering along the $\langle 11\bar{2} \rangle$ direction of the Ni substrate. Scattering in a high symmetry direction of the substrate results in scattering in a high symmetry direction of the adsorbate lattice for only one adsorbate domain. The inset shows the adsorbate surface Brillouin zone and the two resultant scattering directions in this zone for this substrate direction. The upper curve, (a), is the dipole sum for the domain that contributes scattering in the high symmetry direction of the adsorbate surface Brillouin zone ($\bar{\Gamma}-\bar{X}$). The lower curve, (b), is for the other two domains, which contribute scattering across the adsorbate surface Brillouin zone. The center curve, (c), is the average of the three dipole sums, which was used to fit the data.

dipole sums for the three domains, and therefore the expected dispersion, are quite similar in the range of \mathbf{K} vectors studied. The experimentally determined polarizabilities and singleton frequencies for the symmetric mode were obtained by fitting the dispersion data to dipole sums averaged over the three domains. This assumes that the experimentally observed energy is a superposition of unresolved features due to scattering from one domain in a high symmetry direction and scattering from the two other domains in a direction across the adsorbate Brillouin zone. Because of the similarities in the expected dispersion for the two scattering directions, we feel that this approach is justified.

The polarizabilities that we determine seem rather high, on the order of 1.5 to 3 times higher than the polarizabilities determined for adsorbed CO on other surfaces.^{21,20,31,32} The greater polarizability of NO could be the result of NO having one more electron than CO, occupying a π^* orbital. On the other hand, there may be other types of dynamic coupling involved in the dispersion than just through-space dipole coupling. Moskovits and Hulse³³ have shown that dynamic coupling through substrate lattice vibrations can lead to contributions to coverage vs frequency shifts of the same magnitude as that expected for dipole coupling. While their work treated only vibrational coupling in detail, there are other types of dynamic coupling possible through the metal lattice, such as modification of the Ni conduction band electron density in the presence of a vibrating adsorbed species.³⁴ This could be interpreted as the dynamic analog of the well known static chemical effect in the coverage vs frequency

shift. The dipole coupling model takes this into account to some extent, through coupling of image and adsorbate dipoles. However, calculation of the dispersion behavior for this type of coupling would necessitate more detailed knowledge of the spatial dependence of the interaction.

As mentioned in the introduction, the frequency shift of the internal stretch mode in these systems is usually thought of as a combination of a static chemical shift and a dynamic upward shift due to dipole or other coupling between adsorbates. Isotopic mixing experiments are in general a convenient method of separating these two contributions to the frequency vs coverage curve. In the dilution limit of one isotopic species, the vibrations of that species are essentially decoupled due to the differing isotopic vibrational frequencies, but the chemical environment is unchanged. Unfortunately we found NO to be quite labile, rapidly forming mixed isotope species in a mixing chamber when $^{15}\text{N}^{18}\text{O}$ and $^{14}\text{N}^{16}\text{O}$ were combined, even at pressures as low as 10 Torr. We have found the fitting of dispersion curves to be a convenient alternative method of determining ω_0 , the frequency of an adsorbed molecule in the absence of dipole coupling. Within the dipole coupling model, ω_0 is independent of the other parameters, and depends only on the geometry of the lattice used to calculate the dipole sum. Equation (2) shows that ω_0 is the stretching frequency at the value of \mathbf{K} where $\Sigma(\mathbf{K})$ passes through zero. Thus the stretching frequency of isolated NO molecules in the static chemical environment of a 0.5 ML chemisorbed overlayer of NO would be expected to be 185.9 meV, and that of isolated NO in the chemical environment of a 0.4 ML NO overlayer would be expected to be 184.2 meV. The frequencies of the NO stretch for the 0.5 and 0.4 ML coverages are 196 and 193.5 meV, respectively, indicating that there is a frequency shift of approximately 10 meV due to dipole coupling alone at both these coverages.

V. CONCLUSION

To summarize, we have observed a new vibrational mode of NO adsorbed on the Ni(111) surface. This mode is a frustrated translation parallel to the surface of an NO molecule adsorbed in a threefold hollow site in the $c(4\times 2)$ overlayer. Information on such low energy modes is important because of the role these modes play in determining the dynamical behavior of adsorbates, such as surface diffusion, thermal desorption, and the vibrational dephasing of higher energy vibrations. We have measured the dispersion of this mode and found it to be dispersionless. We note a trend in the small but growing database of vibrational frequencies for frustrated translations parallel to the surface, suggesting that the frequencies of these modes may be indicative of their local adsorption geometry. These frequencies may be a better guide to the local adsorption geometry of adsorbates than their intramolecular stretch frequencies, which have recently been shown to be much harder to interpret than previously appreciated.^{1,14,19} We also report the dispersion of the dipole active NO internal stretch mode on this surface, and fit this dispersion with a model of which assumes dipole-dipole coupling between adsorbates. We report experimentally de-

termined polarizabilities, and show that dispersion measurements are a convenient method for determining singleton frequencies, the frequency of an adsorbate in the static chemical environment of the coverage in question, but without the contribution to the frequency shift caused by dynamic dipole coupling.

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- ¹N. Materer, A. Barbieri, D. Gardin, U. Starke, J. D. Batteas, M. A. Van Hove, and G. A. Somorjai, *Phys. Rev. B* **48**, 2859 (1993).
- ²H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, *Surf. Sci.* **65**, 235 (1977).
- ³M. Bertolo and K. Jacobi, *Surf. Sci.* **226**, 207 (1990).
- ⁴D. E. Eastman and J. E. Demuth, *Jpn. J. Appl. Phys. Suppl.* **2**, Pt. 2, 827 (1974).
- ⁵M. J. Breitschafter, E. Umbach, and D. Menzel, *Surf. Sci.* **109**, 493 (1981).
- ⁶H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, *Surf. Sci.* **50**, 296 (1975).
- ⁷H. -P. Steinrück, C. Schneider, P. A. Heimann, T. Pache, E. Umbach, and D. Menzel, *Surf. Sci.* **208**, 136 (1989).
- ⁸F. P. Netzer and T. E. Madey, *Surf. Sci.* **110**, 251 (1981).
- ⁹S. Lehwald, J. T. Yates, Jr., and H. Ibach, in *Proc. IVC-8, ICSS-4, ECOS-3, Cannes, 1980*, edited by D. A. Degras and M. Costa (Le Vide, Les Couches Minces, Suppl. **201**, 221 (1980)).
- ¹⁰W. Erley, *Surf. Sci.* **205**, L771 (1988).
- ¹¹W. Erley and B. N. J. Persson, *Surf. Sci.* **218**, 494 (1989).
- ¹²M. C. Asensio, D. P. Woodruff, A. P. Robinson, K. -M. Schindler, P. Gardner, D. Ricken, A. M. Bradshaw, J. C. Conesa, and A. R. González-Elipe, *J. Vac. Sci. Technol. A* **10**, 2445 (1992).
- ¹³S. Aminopirooz, A. Schmalz, L. Becker, and J. Haase, *Phys. Rev. B* **45**, 6337 (1992).
- ¹⁴L. D. Mapledoram, A. Wander, and D. A. King, *Chem. Phys. Lett.* **208**, 409 (1993).
- ¹⁵D. P. Woodruff, B. E. Hayden, K. Prince, and A. M. Bradshaw, *Surf. Sci.* **123**, 397 (1982).
- ¹⁶W. Menezes, P. Knipp, G. Tisdale, and S. J. Sibener, *Phys. Rev. B* **41**, 5648 (1990).
- ¹⁷N. V. Richardson and A. M. Bradshaw, *Surf. Sci.* **88**, 255 (1979).
- ¹⁸J. S. Ha and S. J. Sibener, *Surf. Sci.* **256**, 281 (1991).
- ¹⁹M. E. Davila, M. C. Asensio, D. P. Woodruff, K. -M. Schindler, Ph. Hofmann, K. -U. Weiss, R. Dippel, P. Gardner, V. Fritzsche, A. M. Bradshaw, J. C. Conesa, and A. R. González-Elipe, *Surf. Sci.* **311**, 337 (1994).
- ²⁰G. D. Mahan and A. A. Lucas, *J. Chem. Phys.* **68**, 1344 (1978).
- ²¹B. Voigtländer, D. Bruchmann, S. Lehwald, and H. Ibach, *Surf. Sci.* **225**, 151 (1990).
- ²²C. D. Peterson and S. D. Kevan, *J. Chem. Phys.* **94**, 2281 (1991).
- ²³R. Berndt, J. P. Toennies, and Ch. Wöll, *J. Elect. Spectrosc. Relat. Phenom.* **44**, 183 (1987).
- ²⁴A. M. Lahee, J. P. Toennies, and Ch. Wöll, *Surf. Sci.* **177**, 371 (1986).
- ²⁵G. Kisters, J. G. Chen, S. Lehwald, and H. Ibach, *Surf. Sci.* **245**, 65 (1991).
- ²⁶J. P. Toennies, Ch. Wöll, and G. Zhang, *J. Chem. Phys.* **96**, 4023 (1992).
- ²⁷G. Witte, H. Range, J. P. Toennies, and Ch. Wöll, *J. Elect. Spectrosc. Relat. Phenom.* **64/65**, 715 (1993).
- ²⁸*CRC Handbook of Chemistry and Physics*, 62nd ed. edited by R. C. Weast (CRC, Boca Raton, 1981).
- ²⁹S. J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes* (Elsevier, Amsterdam, 1968).
- ³⁰F. Hund, *Z. Phys.* **99**, 217 (1936).
- ³¹S. Anderson and B. N. J. Persson, *Phys. Rev. Lett.* **45**, 1421 (1980).
- ³²E. Escalona Platero, S. Coluccia, and A. Zecchina, *Surf. Sci.* **171**, 465 (1986).
- ³³M. Moskovits and J. E. Hulse, *Surf. Sci.* **78**, 397 (1978).
- ³⁴M. Moskovits (private communication).