

# Shape resonance enhancement of vibrational excitations for CO chemisorbed on Ni(111) probed via inelastic electron scattering

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This paper examines how the formation of a transient negative ion during the scattering of an electron from CO chemisorbed on Ni(111) can lead to significant enhancement in the probability for vibrationally inelastic scattering. We specifically report on the incident energy dependence for transient negative ion formation for a  $c(4\times 2)$  overlayer. The signature for this resonance is the energy dependence of the probability for vibrationally inelastic scattering from the CO intramolecular stretch and a CO frustrated rotation, both broadly peaking in the vicinity of 18 eV. Additional support for this scattering mechanism comes from the monotonic rise in scattering intensity for both of these vibrational modes as the final (detector) angle moves towards the surface normal under otherwise fixed kinematic conditions. We also observe the presence of weak first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. All of the aforementioned observations are consistent with the formation of a  $\Sigma$  shape resonance which is slightly lower in energy, and has a shortened lifetime, than in the gas phase. We also report dispersion measurements along the  $\langle 11\bar{2} \rangle$  direction for the  $c(4\times 2)$  structure, as well as for a saturated  $(\sqrt{7}/2 \times \sqrt{7}/2) R19.1^\circ$  CO/Ni(111) overlayer which give information about intermolecular couplings in these compressed structures. Discussions are presented, including wave packet arguments, which emphasize that the presence (or absence) of vibrational excitation in a given vibrational coordinate following negative ion formation can be used to infer important details about femtosecond nuclear coordinate evolution for the system in the excited state.

## INTRODUCTION

Resonantly enhanced inelastic electron scattering is becoming a powerful tool for probing the structure and dynamical properties of adsorbed molecules.<sup>1,2</sup> The classic review articles of Schulz<sup>3,4</sup> provide a rather remarkable tutorial on the origin and characteristics of such “temporary negative ions” in the gas phase. These articles, and the work referenced therein, provide a solid framework for initiating studies of adsorbed species. One of the central issues in this area of endeavor concerns how the properties of such resonances differ from those found in an isotropic ensemble in the gas phase. For example, the presence of a nearby and strongly interacting interface can significantly modify the angular characteristics for injection into and emission from such transient states—with such angular distributions containing important information on the symmetry of the resonance as well as adsorbate geometry. Strong bonding interactions, such as those which occur upon molecular chemisorption, can also lead to large energy level shifts (including the disappearance of low lying resonances), changes in width, and significantly shortened lifetimes for such transient states.

From the point of view of chemical physics, further motivation for conducting scattering measurements involv-

ing negative ion resonances is that they may enable us to probe the short-time, i.e., femtosecond dynamics of transiently formed negative ions on surfaces. Wave packet arguments suggest that we can obtain information about the short-time temporal evolution for adsorbed systems by: (i) observing *which* intramolecular and molecule–surface vibrational modes become excited following transient negative ion formation; and (ii) quantifying the extent to which the characteristic overtone progressions are truncated with respect to gas phase behavior for the rotational and vibrational modes which couple to the scattering process.<sup>5</sup> Another hope is that electrons scattering by such resonant processes will be able to couple with normally forbidden spectroscopic transitions, or those which have minimal scattering cross sections for more conventional interrogation via dipole and impact scattering, yielding new information on the potential energy surfaces for adsorbed species.

Under resonant scattering conditions, the incident electron is attached to a quasibound state of the molecule/surface system. Shape resonances, which involve injection of the incident electron into a previously unoccupied orbital of the adsorbate without further modification of the core electron distribution, are particularly attractive for such studies. Here, e.g., if the electron is placed in an antibonding orbital of the adsorbate, the internuclear separation of the negative ion state will be extended relative to that of the ground state. When the electron escapes, the molecule is abruptly returned to the ground state with modified nuclear coordinates and consequently may be vi-

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brationally or rotationally excited. Strong overtone progressions may also be present for specific normal modes depending on several factors, including the relative position and shape of the excited state (negative ion) potential relative to that of the ground state, as well as the lifetime of the resonance.

Such shape resonances have been observed for various physisorbed<sup>1,2,6-9</sup> and chemisorbed<sup>1,2,10-14</sup> molecules on surfaces. Our initial measurements have focused on the  $c(4\times 2)$ -CO-Ni(111) system. In the gas phase, CO is known to have at least two major shape resonances—a  ${}^2\Pi$  resonance residing at relatively low energy ( $1 < E_i < 3$  eV) (Ref. 15), and a  ${}^2\Sigma$  resonance at higher energy ( $16 < E_i < 23$  eV).<sup>16,17</sup> Chutjian *et al.*<sup>16</sup> performed crossed molecular beam–electron beam measurements on CO and observed broad peaking of the ratio of the scattered intensity for  $\nu=1$  excitation to that for elastic scattering near  $E_i=20$  eV, indicating a resonant excitation process in the energy range 15–25 eV. This was initially attributed to formation of many doubly excited states of  $\text{CO}^-$ . Subsequent and more detailed vibrational inelastic scattering measurements by Tronc *et al.*<sup>17</sup> confirmed the existence of such a high lying resonance, basing their conclusion on the clear observation of vibrationally enhanced scattering at an impact energy of 19.5 eV (with a width of 7 eV). Angularly resolved inelastic scattering measurements confirmed this as a  ${}^2\Sigma$  molecular shape resonance, formed by attachment of an electron to the unoccupied  $2p\sigma_u^*$  (i.e.,  $6\sigma$ ) orbital of CO, which decays via a partial wave channel which has significant  $f$ -wave ( $l=3$ ) character.<sup>17</sup> Recent surface studies have also probed these resonances. For example, Jensen and Palmer<sup>18</sup> have observed enhancement of the  $\nu=0-1$  intramolecular stretch mode for CO physisorbed on graphite at incident energies consistent with those for both the  ${}^2\Pi$  and  ${}^2\Sigma$  resonances of CO. In this case, the  ${}^2\Sigma$  resonance was at 19 eV, just slightly lower than in the gas phase. They also showed, based on angular distribution measurements, that orientationally ordered CO molecules within a commensurate monolayer have their molecular axes approximately parallel to the surface, with some evidence for out-of-plane tilting. (Information on molecular orientation and negative ion symmetry for adsorbed species can most readily be extracted from such measurements when one partial wave dominates the cross section.<sup>19</sup>) Demuth *et al.*<sup>6</sup> have also seen clear evidence of the lower lying resonance for CO physisorbed on polycrystalline Ag. [Very recent work by Jacobi and co-workers on crystalline Ag(111) (Ref. 20) discusses the possible quenching of this state; other interpretations of their results are also possible.<sup>2</sup>] Jacobi *et al.*<sup>20</sup> have also studied resonance scattering from CO overlayers of varying thickness physisorbed on Ag(111), finding significant overtone intensity for CO when intermediate rare gas layers were placed between CO and the substrate, as well as for thick films (8 L deposition), but not for CO monolayers. Sanche and Michaud<sup>21</sup> have also studied resonant scattering from CO in the condensed state, with the resonance falling at about 19 eV. Finally, the most relevant investigation to the present study is that for CO chemisorbed on Ni(110).<sup>22-24</sup> Here, a

broad resonance was seen centered at 18 eV, i.e., shifted downwards from the gas phase value by about 1.5 eV. The downward trend in the position of the resonance in going from the gas phase to the condensed state to, ultimately, a chemisorbed system is most likely due to screening effects, in our case, primarily involving interaction of the transient negative ion with its image in the Ni(111) substrate and the surrounding environment.

In this paper, we report the resonant enhancement of inelastic scattering from two vibrational modes for CO chemisorbed on Ni(111). These modes are the CO intramolecular stretch and one of the low energy frustrated rotations<sup>25</sup> for CO in a  $c(4\times 2)$  structure. The primary data consist of incident energy dependent measurements under fixed geometric conditions, final angular distribution measurements under otherwise fixed kinematic conditions, and preliminary measurements of first overtone scattering from the CO stretch under resonant conditions. It will be shown that the electron energy loss intensities of both modes were found to peak broadly around  $E_i=18$  eV, presumably due to scattering into a  $\Sigma$  shape resonance at this energy. The intensities of scattering from these modes also increased as the final scattering angle was moved towards the surface normal, consistent with a  $\Sigma$  type resonance and the molecular axis being aligned normal to the surface plane, providing further confirmation of the postulated scattering mechanism. To our knowledge, these measurements are the first to demonstrate that a *molecule–surface* mode can be excited for a chemisorbed system as a consequence of resonant electronic excitation. These results join those of Jacobi and Bertolo,<sup>26</sup> who observed excitation of the molecule–surface stretch for  $\text{N}_2$  physisorbed on Al(111), in showing that various molecule–surface modes can be excited under resonant scattering conditions. Such observations, given appropriate calculations, can be used to examine quantitatively the short-time dynamics of adsorbed molecules.<sup>5,27-29</sup> However, even without such calculations, one can learn much about nuclear coordinate evolution by simply taking note of which vibrational modes become excited (and which do not become excited) following resonant excitation.

## EXPERIMENT

The experiments were performed in an ion pumped stainless steel ultrahigh vacuum (UHV) chamber (base pressure of  $5\times 10^{-11}$  Torr) equipped with a high resolution electron energy loss (HREELS) spectrometer for performing inelastic electron scattering measurements, low energy electron diffraction (LEED) for assessing surface order and overlayer structure, a double pass cylindrical mirror analyzer for Auger measurements of surface cleanliness, a quadrupole mass spectrometer for residual gas analysis and thermal desorption measurements, and an ion sputter gun for sample preparation. The HREELS spectrometer consists of a two-stage monochromator and a single-stage analyzer which are based on  $127^\circ$  cylindrical deflection optics.<sup>30,31</sup> The analyzer rotates independently in the plane defined by the incident electron beam and the surface normal. Detector motion covers a range of  $55^\circ$ , for

a total included 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. This arrangement permits scattering experiments to be performed at various final wave vectors without varying incident kinematic conditions, a useful configuration for comparing results with scattering calculations. Finally, the incident angle was fixed at  $\Theta_i = 65^\circ$  in order to reach a scattering angle as close as possible to the surface normal ( $\Theta_f = 20^\circ$ ), while still being able to scan the specular beam.

The Ni(111) crystal was cleaned by repeated cycles of  $\text{Ar}^+$  ion sputtering (1 kV, 6  $\mu\text{A}$ ,  $T_s = 300$  K) and annealing at  $T_s = 1150$  K. In this paper, we deal with two different well-ordered CO overlayers—a  $c(4 \times 2)$  overlayer structure which forms at temperatures below 200 K when the CO coverage is  $\Theta_{\text{CO}} = 0.5$ , and a  $(\sqrt{7}/2 \times \sqrt{7}/2) R19.1^\circ$  CO/Ni(111) structure, which forms upon saturated dosing at low temperatures with  $\Theta_{\text{CO}} = 0.57$ . These overlayers are quite complementary for probing adsorbate dynamics. The  $c(4 \times 2)$  overlayer consists of CO bound to the Ni substrate with only one type of coordination. The long-held view, based upon vibrational analysis<sup>32(a)-(d)</sup> is that the CO resides in twofold coordinated bridge sites. Very recent surface extended x-ray absorption fine structure (SEXAFS) and photoelectron diffraction (PED) measurements (see *Note added in proof*) have called this  $c(4 \times 2)$  structural assignment into question, with the SEXAFS and PED measurements favoring bonding at threefold coordinated hollow sites. The  $(\sqrt{7}/2 \times \sqrt{7}/2) R19.1^\circ$  CO/Ni(111) structure has a 3:1 ratio of bridge-bonded to on-top bonded CO molecules.<sup>32(e)-(e)</sup> CO overlayers were prepared by dosing 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 the 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 observed routinely with this growth procedure. Vibrational spectra recorded in the specular direction provided further confirmation of  $c(4 \times 2)$  overlayer growth, as characterized by a CO intramolecular stretch at 234 meV and Ni–CO stretch at 50 meV.

## RESULTS AND DISCUSSION

We begin this section by presenting the primary data which support the existence of a resonant scattering channel for CO chemisorbed on Ni(111). The two characteristic signatures upon which we will focus are (i) the dependence of vibrationally inelastic scattering as a function of incident electron energy, including the enhancement of vibrationally inelastic cross sections for some adsorbate normal modes in the vicinity of 18 eV, and (ii) the angular distributions of the emitted electrons. One should remember that while dipole scattering will peak at the specular angle,<sup>33</sup> resonant scattering will characteristically have a final angular distribution which will depend on both the symmetry of the resonance and the geometry of the

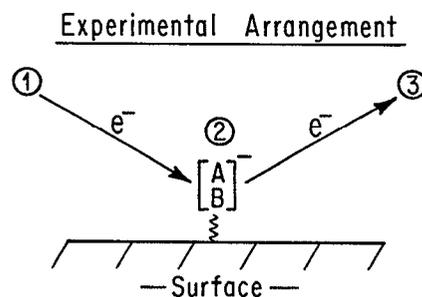


FIG. 1. A schematic view of the three stages which comprise the electronically resonant scattering process: (1) Injection of the incident electron under resonant conditions to form the transiently bound negative ion. Probability of injection depends on electron energy, incident angle, molecular geometry, and symmetry of the resonance. (2) Nuclear coordinates evolve on the excited state (negative ion) potential energy surface, typically for femtosecond time scales, with movement due to the forces generated by the presence of an extra electron in the molecule/surface bonding system. (3) Electron ejection from the transiently formed state. Emitted electron is energy analyzed, as a function of final scattering angle, to examine excitation in both the intramolecular and molecule–surface vibrational degrees of freedom on the ground state potential energy surface. The presence (or absence) of vibrational excitation in a given coordinate gives a snapshot of short time scale nuclear coordinate evolution for the system in the excited state.

adsorbate–substrate system.<sup>2,34,35</sup> Both of these criteria are satisfied by the data, providing support for the formation of a temporary negative ion state whose energy level is broadly peaked around  $E_i = 18$  eV. Further evidence of resonance formation, briefly discussed later in this section, is provided by the observation of (very weak) first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. The apparent truncation of this vibrational progression at the first overtone suggests (given reasonable assumptions about the shape and position of the excited state potential relative to that of the ground state) that the lifetime of this resonance is very short, significantly shorter than in the isolated molecule limit. Figure 1 presents a schematic view of the electronically resonant scattering mechanism which illustrates the three stages upon which we will focus in the following paragraphs: transient negative ion formation via injection into the resonance, nuclear coordinate evolution on the negative ion potential energy surface, and finally electron ejection and detection.

Figure 2 shows a series of HREELS spectra for the  $c(4 \times 2)$  CO overlayer in which the incident energy of the electron beam  $E_i$  was systematically varied between 7 and 30 eV, while the scattering geometry was held constant with  $\Theta_i = 65^\circ$  and  $\Theta_f = 20^\circ$ . The contribution from dipole allowed scattering in this configuration is negligible due to the large angle between the detector and the specular angle. These spectra show the emergence and subsequent disappearance of a loss feature at  $\sim 37.5$  meV, with the signal having a broad maximum peaking at about  $E_i = 18$  eV. This 37.5 meV loss peak has been previously assigned as a frustrated rotation of CO on Ni(111) (Ref. 25). This low energy mode may have mixed character due to hybridization with a nearly degenerate zone-edge surface phonon mode on Ni(111).<sup>25,31</sup> Figure 3 shows a similar collection of HREELS spectra, but for the energy loss range which

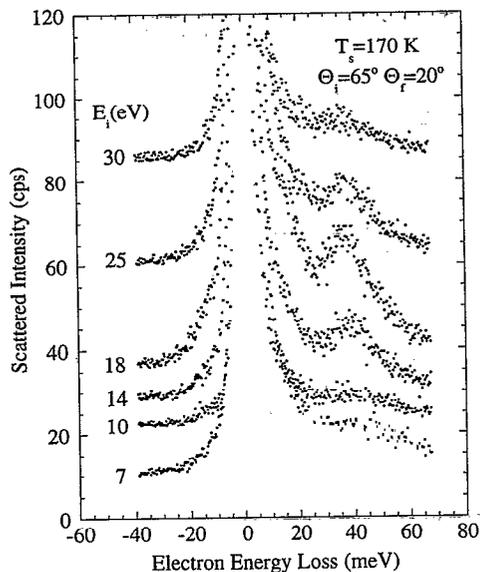


FIG. 2. Incident energy  $E_i$  dependence of the electron energy loss spectra for  $c(4 \times 2)$ -CO-Ni(111) at  $T_s = 170$  K with  $7 < E_i < 30$  eV. Enhancement of the spectral feature for the frustrated rotation of CO (37.5 meV) in the vicinity of  $E_i = 18$  eV is due to the formation of a transient negative ion shape resonance. Measurements were done with fixed scattering geometry  $\Theta_i = 65^\circ$  and  $\Theta_f = 20^\circ$  along the  $\langle 11\bar{2} \rangle$  direction. Spectral accumulation times per channel: 14, 18, and 25 eV—5 s, 10 and 30 eV—7 s; 7 eV—7.5 s.

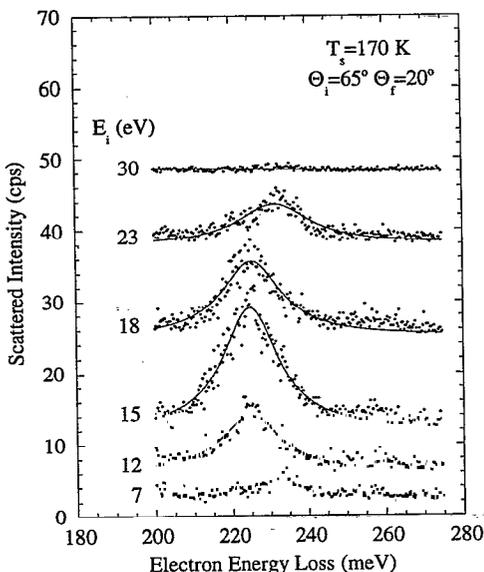


FIG. 3. Incident energy  $E_i$  dependence of the electron energy loss spectra for  $c(4 \times 2)$ -CO-Ni(111) at  $T_s = 170$  K with  $7 < E_i < 30$  eV. Enhancement of the spectral feature for the C-O internal stretch in the vicinity of  $E_i = 18$  eV is due to the formation of a transient negative ion shape resonance. Measurements were done with fixed scattering geometry  $\Theta_i = 65^\circ$  and  $\Theta_f = 20^\circ$  along the  $\langle 11\bar{2} \rangle$  direction. Peak position shifts are due to mode dispersion (see Fig. 12). Solid lines are Lorentzian fits to assist viewing. Spectral accumulation times per channel were 10 s for 30 eV and 5 s for all other energies.

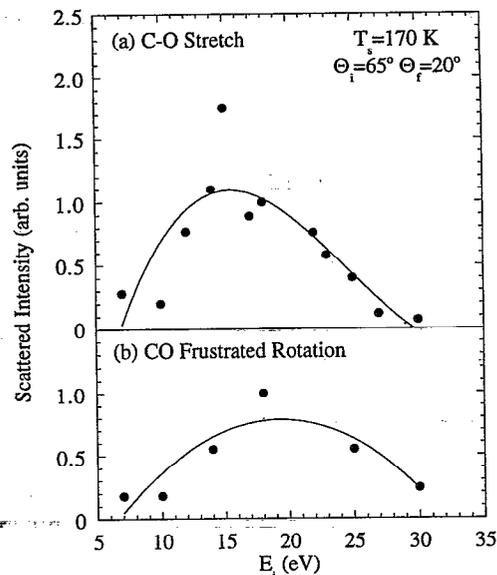


FIG. 4. Energy dependence of shape resonance scattering leading to enhanced excitation of (a) CO intramolecular stretch and (b) CO frustrated rotation normal modes. Solid lines are fits to assist viewing. Integrated peak intensities are plotted for CO in a  $c(4 \times 2)$ -CO-Ni(111) structure. The electron scattering geometry was fixed at  $\Theta_i = 65^\circ$  and  $\Theta_f = 20^\circ$  along the  $\langle 11\bar{2} \rangle$  direction.

encompasses the CO intramolecular stretch. At  $E_i = 7$  eV, a small peak is observed at 234 meV which is about 1/100 of the intensity for the specular CO intramolecular stretch. As the incident beam energy is scanned, we again see the characteristic incident energy dependent enhancement of inelastic scattering in the vicinity of 18 eV. These data are reminiscent of those previously reported for the CO/Ni(110) system.<sup>22-24</sup> (We also see some movement of the peak position as the beam energy is changed which is due to mode dispersion; as expected, this is not accompanied by any change in the frequency observed at the specular angle. Moreover, the added widths seen for these peaks may be due to concurrent excitation of low energy librations and/or phonon modes—we unfortunately did not have the resolution to address this issue. This possibility has been discussed previously for the case of condensed CO films.<sup>21</sup>) Figure 4 summarizes the above findings, for both the frustrated rotation and intramolecular stretch modes, by plotting the probability of vibrationally inelastic scattering vs incident beam energy. The results for both of these measurements are, within experimental uncertainties in the data, identical—giving strong evidence for a broad negative ion state that is slightly lower in energy than the documented  $^2\Sigma$  resonance for gas phase CO.<sup>17</sup>

Tronc *et al.*<sup>17</sup> observed resonant enhancement of vibrationally inelastic scattering from gas phase CO at 19.5 eV with an impact energy width of about 7 eV, i.e.,  $16 < E_i < 23$  eV. The data shown in Fig. 4 have a width of  $\sim 15$  eV, approximately twice as wide as in the gas phase. This is not surprising given the smaller lifetime that would be expected for a transient negative ion state of a chemisorbed molecule on a metallic substrate.

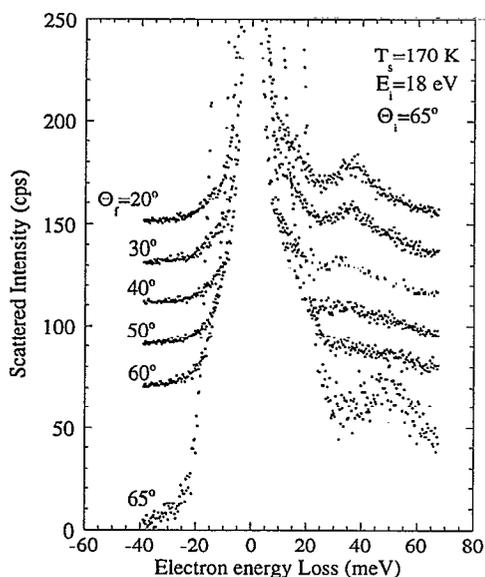


FIG. 5. Final scattering angle ( $\Theta_f$ ) dependence of the electron energy loss spectra for  $c(4 \times 2)$ -CO-Ni(111) at  $T_s=170$  K along the  $\langle 112 \rangle$  direction with  $E_i=18$  eV and  $\Theta_i=65^\circ$ . The intensity of the spectral feature due to the frustrated rotation of CO (37.5 meV) increases monotonically as the final scattering angle approaches the surface normal. This enhancement is consistent with that expected for scattering involving a  $\Sigma$  shape resonance at this incident energy. (Note that the dipole allowed C-Ni stretch appears at  $\sim 50$  meV under specular conditions  $\Theta_i=\Theta_f=65^\circ$ .) Spectral accumulation times per channel—1.5 s for  $65^\circ$  and 5 s for all other angles.

Additional and very informative information about the scattering mechanism comes from the angular distributions for electrons emitted under resonant “injection” conditions. Such data is shown in Figs. 5 and 6 for the low energy (adsorbate frustrated rotation) and high energy (adsorbate intramolecular stretch) electron energy loss regimes, respectively. For the data shown in these figures, we held the incident energy and incident angle fixed at  $E_i=18$  eV and  $\Theta_i=65^\circ$ , and varied the final scattering angle from  $20^\circ$  to  $65^\circ$ .

In Fig. 5, we show at  $\Theta_f=65^\circ$  (the specular angle) a 50 meV energy loss peak which is the dipole allowed Ni-CO stretch. As  $\Theta_f$  is systematically moved towards the surface normal, a new peak appears at 37.5 meV, which, as previously discussed, is assigned to a frustrated rotation. The intensity of this peak increases monotonically as  $\Theta_f$  approaches the surface normal. This behavior, shown graphically in Fig. 7(b), is consistent with scattering involving a  $\Sigma$  resonance in which the molecular axis is perpendicular to the surface plane. (We also note that the data in Fig. 5 may suggest the presence of a second feature that is obscured in the energy loss side of the diffuse elastic peak. Unfortunately, the quality of the data does not allow us to definitely assign this to enhancement of a frustrated translation as opposed to changing multiphonon contributions to the scattering.)

Figure 6 shows a series of energy loss spectra in the CO stretch regime which map out the final angular distribution for inelastically scattered electrons under fixed incident,

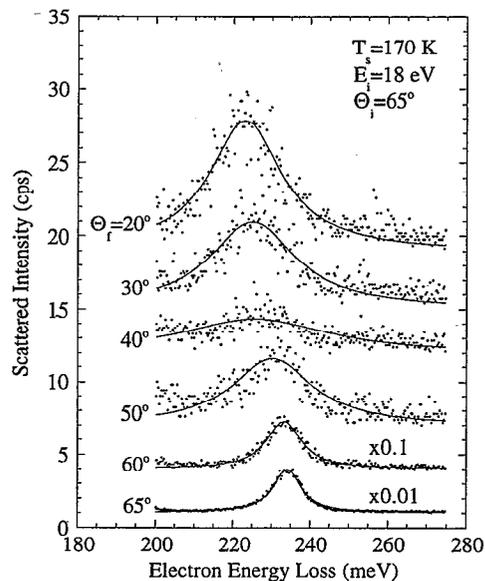


FIG. 6. Final scattering angle ( $\Theta_f$ ) dependence of the electron energy loss spectra for  $c(4 \times 2)$ -CO-Ni(111) at  $T_s=170$  K along the  $\langle 112 \rangle$  direction with  $E_i=18$  eV and  $\Theta_i=65^\circ$ . The intensity of the spectral feature due to the intramolecular stretch of CO increases monotonically as the final scattering angle approaches the surface normal. This enhancement is consistent with that expected for scattering involving a  $\Sigma$  shape resonance at this incident energy. Spectral accumulation times per channel:  $65^\circ$ —1.5 s;  $60^\circ$ —2 s;  $50^\circ$ —5 s;  $40^\circ$ —7 s;  $30^\circ$ —7 s;  $20^\circ$ —5 s.

and electronically resonant, kinematic conditions. (The frequency dispersion of these loss peaks is due to CO-CO intermolecular interactions and will be discussed later in this paper.) The composite angular distribution compiled from these spectra is shown in Fig. 7(a). Here we again see a smooth increase in scattering intensity as  $\Theta_f$  approaches the surface normal. However, unlike the distribution shown in Fig. 7(b), we also see a (much stronger) intensity lobe which peaks at the specular angle—expected behavior for the dipole allowed CO intramolecular stretch transition. Taken together, the data presented in panels (a) and (b) of Fig. 7 lend strong support to a scattering mechanism involving a  $\Sigma$ -type molecular resonance.

Another feature of electronically resonant scattering, typically seen in the gas phase, is the presence of a strong overtone progression in vibrational energy loss spectra.<sup>1,2,4</sup> One can envision this overtone progression as (indirectly) mapping out temporal evolution of the initially formed wave packet on the excited state potential energy surface, as shown schematically in Fig. 8. In this view, the excited state wave packet evolves on the negative ion potential energy surface and subsequently decays back to the ground state, leaving the molecules with a distribution of final vibrational states whose details depend critically on the excited state lifetime, as well as the shapes and relative positions of the ground and excited electronic surfaces. Gadzuk has written extensively on the details of this process.<sup>5,27-29</sup> We also reiterate that the presence (or absence) of vibrational excitation in a given coordinate gives a snap-

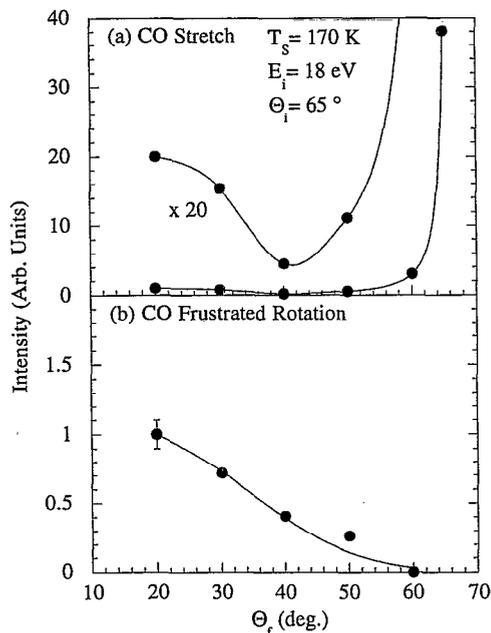


FIG. 7. Angle dependence of the emitted electron following injection into the CO  $\Sigma$  shape resonance at  $E_i=18$  eV. The angular distributions for electrons coupling to either the CO intramolecular stretch (top panel) or CO frustrated rotation (lower panel) peak along the CO internuclear axis, i.e., normal to the surface. These angular distributions are consistent with those expected for scattering involving a CO  $\Sigma$  shape resonance. (The CO stretch also peaks at the specular angle due to dipole allowed scattering.)

shot of short time scale nuclear coordinate evolution for the system in the excited state.

Figure 9 presents two energy loss spectra, taken under resonant scattering conditions ( $E_i=18$  eV,  $\Theta_i=65^\circ$ , and  $\Theta_f=20^\circ$ ), which demonstrate the presence of the first overtone signal arising from the CO intramolecular

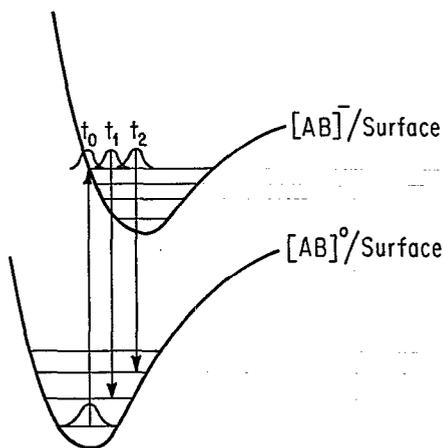


FIG. 8. A schematic wave packet diagram for transient negative ion scattering which illustrates femtosecond time scale propagation on the excited potential energy surface. The resulting overtone progression on the ground state contains information on the negative ion lifetime. For simplicity, not all Franck-Condon transitions are shown.

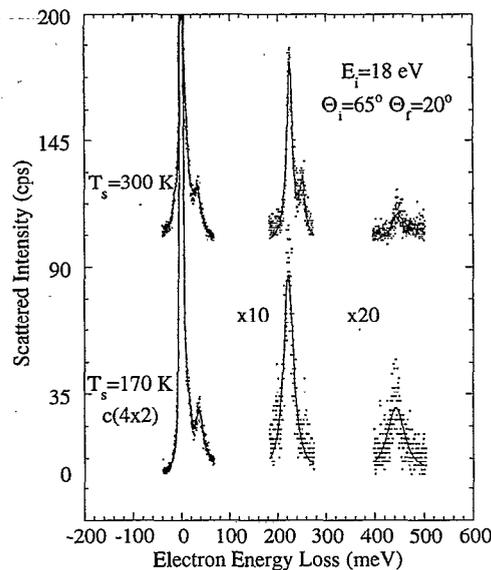


FIG. 9. Evidence for overtone scattering along the  $\langle 11\bar{2} \rangle$  direction involving the CO intramolecular stretch under resonant scattering conditions. The upper spectrum is for an overlayer prepared by warming a  $c(4\times 2)$  structure from  $T=170$ – $300$  K. This structure contains an admixture of bridge-bonded and on-top bonded CO molecules which explains the presence of two peaks in the vicinity of 220–260 meV. The lower spectrum is for a  $c(4\times 2)$  structure. The truncation of the progression at the first overtone is due primarily to the shortened lifetime of the resonance for chemisorbed CO vs that in the gas phase; the spectrum may also be influenced by energy loss dependent sensitivity changes in the spectrometer. Accumulation times per channel for the three spectral regions (elastic,  $n=0\rightarrow 1$ , and  $n=0\rightarrow 2$ ): 170 K—5, 5, and 10 s, respectively; and 300 K—5, 10, and 24 s, respectively.

stretch. Data are shown for a low temperature ensemble in a  $c(4\times 2)$  structure, as well as for a room temperature ensemble which contains an equilibrium admixture of on-top and bridge-bonded species (plus, perhaps, some three-fold coordinated species). The apparent truncation of the CO stretch progression at the first overtone (given the small cross section, we did not have sufficient sensitivity to find the next overtone) attests to the very short lifetime of the resonance for chemisorbed CO, with our  $I(\nu=1)/I(\nu=2)$  ratio being larger than the gas phase value. Even in the gas phase, this CO resonance is relatively short lived, having  $I(\nu=1)/I(\nu=2)$  and  $I(\nu=1)/I(\nu=3)$  cross section ratios of 6/1 and 22/1 at  $E_i=19.5$  eV, respectively.<sup>17</sup> (Overtone ratios for condensed CO films<sup>21</sup> and for CO physisorbed on graphite<sup>18</sup> are quite similar to those in the gas phase.) Combining such overtone data with other information, namely knowledge of the shape of the excited state potential and its position with respect to that for the ground state, one can quantify the lifetime of the excited state. Such wave packet calculations are not yet available for this system.

The final group of measurements we wish to report deal with intermolecular interactions between adsorbed CO molecules. These interactions can be assessed by measuring the wave vector dependent energy dispersion for the CO intramolecular stretch. We report such measurements along the  $\langle 11\bar{2} \rangle$ , i.e.,  $\bar{\Gamma}\bar{M}$  symmetry direction of Ni(111),

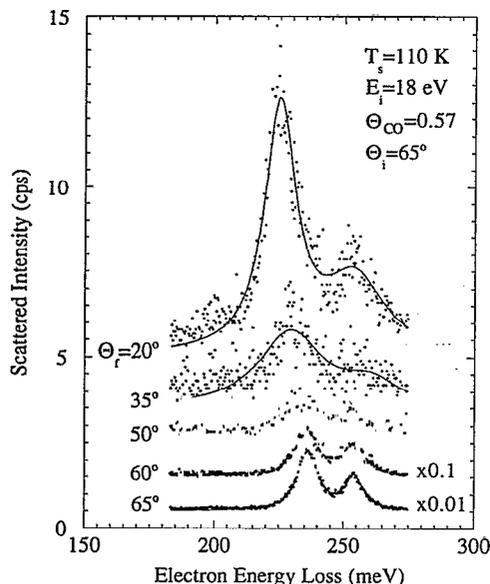


FIG. 10. Final scattering angle ( $\Theta_f$ ) dependence of the electron energy loss spectra for a saturated ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) structure which has a 3:1 ratio of bridge-bonded to on-top bonded CO molecules. The angle dependencies of the CO intramolecular stretch peaks contain information about intermolecular interactions and form the basis of the dispersion curves plotted in Fig. 11. Solid lines are nonlinear least squares fits with two Lorentzian functions.

for two different overlayers—a  $c(4 \times 2)$  overlayer, and a CO saturated ( $\Theta_{\text{CO}}=0.57$ ) ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) overlayer which contains a 3:1 admixture of bridge-bonded to on-top bonded CO molecules. These measurements complement our earlier study of wave vector dependent dispersion for one of the CO frustrated translation modes of the  $c(4 \times 2)$  system.<sup>25</sup> We also note that we have referenced  $\Delta K_{\parallel}$  for these measurements, which were performed here under resonant conditions, with respect to the incident beam. This was possible due to the short lifetime of the  $2\Sigma$  CO shape resonance, i.e., memory of the incident state was not lost since “dephasing” interactions are substantially slower than the lifetime of the resonance, as is the energy relaxation lifetime for this mode.<sup>36</sup> Figure 10 shows a series of spectra for the ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) overlayer which reveals that bridge-bonded molecules have significant dispersion as data is collected further into the surface Brillouin zone (SBZ), whereas the data for on-top sited molecules are dispersionless. This behavior can be seen clearly in Fig. 11, which presents dispersion data for the two different overlayers. The dispersion curves for more highly coordinated molecules, whether in the  $c(4 \times 2)$  or ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) structures, exhibit essentially the same behavior—with the frequency systematically decreasing as  $\Delta K_{\parallel}$  is increased out towards the edge of the SBZ. This dispersion is due to strong CO dipole-dipole interactions within the adsorbate layer, and is reminiscent of earlier work on  $c(2 \times 2)$ -CO-Cu(100) (Ref. 38) and  $(2 \times 1)$ -CO-Ni(110) (Ref. 39), which also showed  $\sim 5\%$  frequency changes across the SBZ. As noted above, the

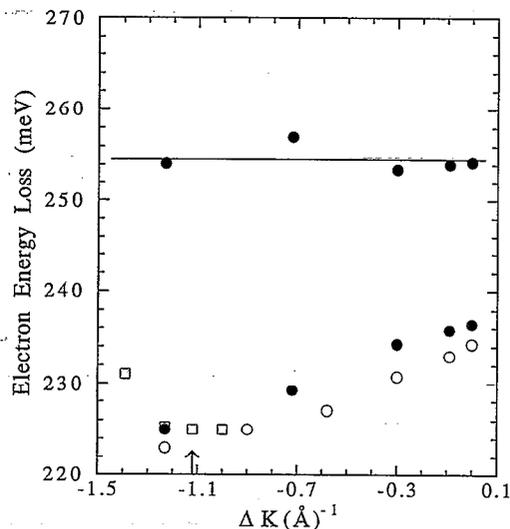


FIG. 11. Dispersion curves for the CO intramolecular stretch for two different overlayer structures. Open circles are for a  $c(4 \times 2)$ -CO-Ni(111) overlayer at  $T_s=170$  K with  $E_i=18$  eV and  $\Theta_i=65^\circ$ . Filled circles are for bridge-bonded and on-top bonded CO taken from a saturated ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) overlayer at  $T_s=110$  K with  $E_i=18$  eV and  $\Theta_i=65^\circ$ . Open squares are from the incident energy dependent data of Fig. 3. The adsorbate's three-domain-averaged surface Brillouin zone edge is marked by an arrow at  $-1.12 \text{ \AA}^{-1}$  (Ref. 37).

data for on-top sited molecules were dispersionless. We may explain this as being due to the lower density of, and further separation between, on-top sited CO molecules. Similar reasoning was given by Andersson and Persson<sup>38</sup> who observed basically no dispersion for a dilute and disordered CO layer on Cu(100) having about 1/4 of the  $c(2 \times 2)$  coverage. It has also been suggested that the lack of dispersion for on-top sited molecules may be due, in part, to screening by the surrounding sea of bridge-bonded species.<sup>40</sup>

## CONCLUSION

In this paper, we have examined several aspects of how transient negative ion formation can influence the scattering of an electron from a chemisorbed molecule CO/Ni(111). In order to simplify our analyses, most measurements were intentionally carried out on a  $c(4 \times 2)$  overlayer, a structure which consists exclusively of CO bound with one type of coordination. In this study, our primary focus has been on the extent to which formation of a resonant electronic state can influence inelastic scattering probabilities for various vibrational/librational modes of the molecule-surface system. Such measurements are quite important as they contain information on, e.g., the energetic location and width of the excited electronic state, vibrational structure on the ground state potential, and especially the short-time dynamics of the system. We especially wish to reiterate that even without sophisticated scattering calculations, one can learn much about (femtosecond) nuclear coordinate evolution on the excited sur-

face by simply taking note of which vibrational modes become excited—and which do not become excited—following resonant excitation.

In our experiments, we have dealt with a relatively high lying resonance for CO, which is formed by attaching an electron to an antibonding  $2p\sigma_u^*$  (i.e.,  $6\sigma$ ) molecular orbital of CO, leading to the formation of a  ${}^2\Sigma$  molecular shape resonance. This state is believed to decay, primarily, via a partial wave channel which has significant  $f$ -wave ( $l=3$ ) character.<sup>17</sup>

One of the signatures which we observe for this resonance is the incident energy dependence of the probability for vibrational inelastic scattering from the CO intramolecular stretch and a CO frustrated rotation, both broadly peaking in the vicinity of 18 eV. The position of this resonance is somewhat lower than the gas phase value of 19.5 eV, presumably due to screening effects arising from interaction of the negative ion with its image and the surrounding environment. Additional support for this scattering mechanism comes from the monotonic rise in scattering intensity for both of these vibrational modes as the final (detector) angle is moved towards the surface normal under otherwise fixed kinematic conditions. This is the expected behavior for a  $\Sigma$  shape resonance for a molecule oriented perpendicularly to the surface plane. We also observe the presence of first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. All of the aforementioned observations are consistent with the formation of a  $\Sigma$  shape resonance which is slightly lower in energy—and has a shortened lifetime—than in the gas phase. These results provide the first evidence for excitation of a *molecule-surface* normal mode due to electronically resonant scattering from a chemisorbed system. The importance of observations such as this is that they give a glimpse of how the nuclear coordinates for the molecule-surface system evolve on the excited state's potential energy surface. For example, the observation of excitation for the CO intramolecular stretch following resonance formation, including overtone excitation, is consistent with the expected behavior for transient population of an antibonding molecular orbital of the molecule. Here the intramolecular bond begins to elongate during the lifetime of the resonance with vibrational excitation in the final state providing the telltale for this behavior. Similarly, observation of excitation for a frustrated rotation implies that the molecule (which in its ground electronic state already deviates *instantaneously* from its time-averaged upright orientation due to thermally excited librational motion) starts to bend over in the negative ion state, possibly due to attraction towards its image. (See *Note added in proof* for further comments on the geometric orientation of the initial state.) Different spatial anisotropies in the attractive and repulsive parts of the excited state potential, as compared to the neutral electronic surface, may also contribute to rotational reorientation.<sup>41,42</sup> Interactions with such librations may also be influenced by rotationally inelastic electron-molecule scattering cross sections, as noted for gas phase collisions.<sup>21,43,44</sup>

One should note that such resonantly enhanced inelas-

tic scattering measurements provide a nice complement to electron induced desorption experiments for probing the short-time dynamics of molecular adsorbates. Detailed analysis of desorption events, including velocity and final quantum state analysis, can be used to extract information on the dynamical evolution of adsorbed molecules whose geometries evolve into nonbonding orientations. Examples of this include rotational reorientation during the lifetime of an excited state, termed “desorption by electronically stimulated adsorbate rotation” for NO/Pt(111) (Ref. 41), or desorption due to attraction of the transient negative ion into a repulsive region of the ground state potential.<sup>45</sup> Electronically resonant inelastic scattering measurements also add new supporting information to surface photochemistry experiments which, in many instances, actually proceed via attachment of photoexcited electrons originating from the substrate.

Finally, we have presented dispersion measurements for both on-top and bridge-bonded species in a saturated ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) overlayer, for molecules in a simpler  $c(4 \times 2)$  overlayer. These dispersion curves contain information about intermolecular couplings in these structures. These measurements complement our earlier study of wave vector dependent dispersion for one of the CO frustrated translation modes of the  $c(4 \times 2)$  system.<sup>25</sup> Such resonantly enhanced scattering experiments may prove to be of further utility by allowing normal mode frequencies to be observed for vibrational coordinates that typically have cross sections that are too small to permit observation via other, more conventional scattering channels.

Future efforts will attempt to identify systems which live long enough to reveal more extended overtone progressions than observed herein for CO/Ni(111). It is hoped that such overtone progressions will be able to serve as clocks for excited state lifetimes when combined with data from gas phase measurements and wave packet calculations.<sup>5,27-29</sup> Recent theoretical work suggests that longer lived excited states should indeed exist for adsorbates and be experimentally accessible.<sup>46</sup>

*Note added in proof.* Very recent surface extended x-ray absorption fine structure<sup>47</sup> (SEXAFS) and photoelectron diffraction<sup>48</sup> (PED) measurements indicate that the CO molecules may reside in threefold coordinated hollow sites for the  $\theta_{co}=0.5$   $c(4 \times 2)$ -CO-Ni(111) overlayer. These results call into question the long-held view, based upon vibrational analysis,<sup>32(a)-(d)</sup> that this overlayer is comprised of CO molecules bound at twofold coordinated bridge sites. The proposed structure derived from the new SEXAFS measurements would place the adsorbates in rather close proximity to each other, with a closest CO-CO separation of only 2.88 Å. The authors state<sup>47</sup> that interadsorbate repulsions in this structure could be decreased by a slight tilting of the CO molecules away from the surface normal, and that they could not at this time determine to better than  $\pm 10^\circ$  whether the hollow sited CO molecules were oriented along the surface normal. Such tilting of the equilibrium geometry away from the surface normal, if present, would be expected to enhance the probability of

coupling to frustrated rotational excitations during negative ion formation. We also note that the saturated  $\theta_{\text{CO}} = 0.57$  ( $\sqrt{7}/2 \times \sqrt{7}/2$ )  $R19.1^\circ$  CO/Ni(111) overlayer cannot be formed with a 1:3 combination of on-top and threefold hollow sited molecules.<sup>32(c),32(d),47</sup> It therefore seems likely that this overlayer should still be considered to consist of a 1:3 admixture of on-top and bridge-bonded molecules. Other examples of multiply sited<sup>49</sup> and single<sup>50</sup> bonding configurations for CO on Ni(111) at various coverages and temperatures exist in the extensive literature for this system. For example, an early PED study of a ( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$  CO/Ni(111) overlayer demonstrated the presence of only bridge-bonded CO molecules at  $\theta_{\text{CO}} = 0.33$ .<sup>49</sup> Viewed together, such observations imply that CO molecules repeatedly switch their binding sites as coverage is varied from low to saturation values, and emphasize that further improvement in our understanding of interadsorbate and adsorbate-substrate interactions is still needed.

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