

Gauche-Trans Conformational Changes in Ethyl Formate Chemisorbed on Ni(111): Coverage-Dependent RAIRS Spectra

J. Wang, M. Castonguay, J.-R. Roy, E. Zahidi, and P. H. McBreen*

Département de chimie, Université Laval, Québec (Qué), Canada G1K 7P4

Received: September 3, 1998; In Final Form: January 8, 1999

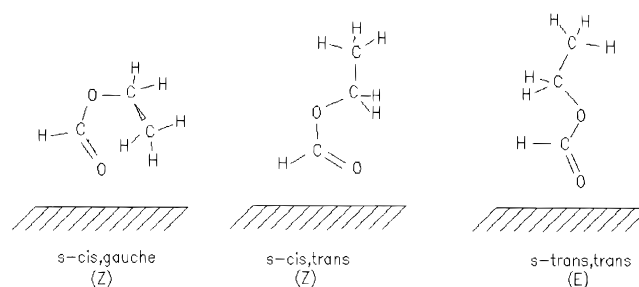
Infrared reflectance spectra of ethyl formate on Ni(111) at 105 K were recorded as a function of surface coverage. The RAIRS activities of several bands are found to vary in a correlated manner as a function of coverage. The activity of both the asymmetric stretching vibration and the twisting vibration of the CH₂ group at low coverages conclusively show that adsorption occurs initially in the *s-cis,gauche* conformation. These two bands fade out on increasing the coverage and are completely removed at full monolayer coverage. The coverage dependence is interpreted in terms of rotational isomerization to a planar conformation as the packing density in the adlayer is increased. The results are consistent with an attribution of the full coverage molecular structure to the *s-trans,trans* conformation.

Introduction

Conformational change in adsorbed layers is of general importance,¹ and the area of heterogeneous asymmetric synthesis is a particularly relevant example. Efficient enantioselective catalysis occurs in a few rare cases on chiral compound modified metal surfaces.² The most studied prochiral substrates are keto ester molecules. The study of simple formic acid esters, such as ethyl formate, is likely to provide information which may be useful in understanding the more complex keto ester systems. The first observation of coverage-dependent conformational change in ethyl formate on Ni(111) was based on vibrational data for methyl formate, ethyl formate, and methyl acetate acquired by Zahidi et al using a narrow band HgCdTe (MCT) detector.^{3,4} The reflectance absorbance infrared spectroscopy (RAIRS) experiment is sensitive to rotational isomerization that involves a significant change in the orientation of some bonds with respect to the metal surface plane. Such changes are most conclusive in the case where rotamerization involves a change in point group symmetry since one cannot assume, a priori, that absolute band intensities are independent of the molecular orientation.⁵ The previous studies^{3,4} revealed evidence for a *s-cis,gauche* conformation at low coverages, followed by rotamerization to either a *s-cis,trans* or a *s-trans,trans* conformation at higher coverages, resulting in a complete removal of the *s-cis,gauche* form at monolayer coverage. The present study provides new information in the form of $\nu(\text{CH})$ vibrational data acquired using an InSb detector, as well as rapid acquisition spectra recorded during gas exposure using the MCT detector.

Hindered rotation around the HCO–OCH₂CH₃ and HCOO–CH₂CH₃ bonds of ethyl formate leads to the possibility of isolating four rotational isomers,^{6,13} three of which are illustrated in Chart 1. Whereas the *s-cis,trans* and *s-trans,trans* isomers display C_s point group symmetry, the *s-cis,gauche* and *s-trans,gauche* forms display C₁ symmetry due to the fact that the ethyl group is rotated out of the HOCO plane. The *s-cis* and *s-trans* families of rotamers are usually referred to as the (Z) and (E) conformations, respectively. The (Z) conformations are the most stable, and the relative populations of the four conformers depend sensitively on the phase under study.^{10–13} The most stable form is the *s-cis,trans* rotamer which is present

CHART 1



exclusively in the pure annealed crystalline solid.¹² Both the *s-cis,trans* and *s-cis,gauche* forms are readily detected in the vapor phase. Ab initio calculations,^{12,13} as well as vibrational^{12,13} and microwave⁸ data, show that the energy difference and rotational barrier between the gas phase *s-cis,trans* and *s-cis,gauche* conformers are around 0.2 and 1.1 kcal mol^{−1}, respectively. Ultrasound dispersion measurements,⁹ Raman spectroscopy studies,¹² and ab initio calculations^{12,13} also indicate that a small proportion of the (E) conformation is present in the liquid phase. The experimentally determined energy difference and rotational barrier for (Z) to (E) conversion in liquid ethyl formate are 2.50 and 3.38 kcal mol^{−1}, and the ab initio determined values are 5.5 and 6.5 kcal mol^{−1}, respectively.¹³

The calculated dipole moments¹³ for the (E) conformations are around 4.5 D, and the experimental values⁸ for the (Z) rotamers, *s-cis,trans* and *s-cis,gauche*, are 1.98 and 1.81 D, respectively. The greater intrinsic stability of the (Z) isomers is in large part due to the antiparallel alignment of the two CO dipoles.¹⁴ Additional intramolecular factors, such as steric and conjugation effects, also contribute to the relative stabilities.¹⁵ Major modifications in conformational equilibria may be imposed by varying a variety of extrinsic parameters. For example, the large difference in dipole moment between the (Z) and (E) forms leads to an enhanced stabilization of the (E) conformations in polar solvents. Thus, NMR studies of ethyl formate in 1:1 mixtures of dimethylformamide and acetone-*d*₆ reveal that the (E) to (Z) enthalpy difference is lowered to 1.67 kcal/mol.¹⁰ Another way in which the relative populations of

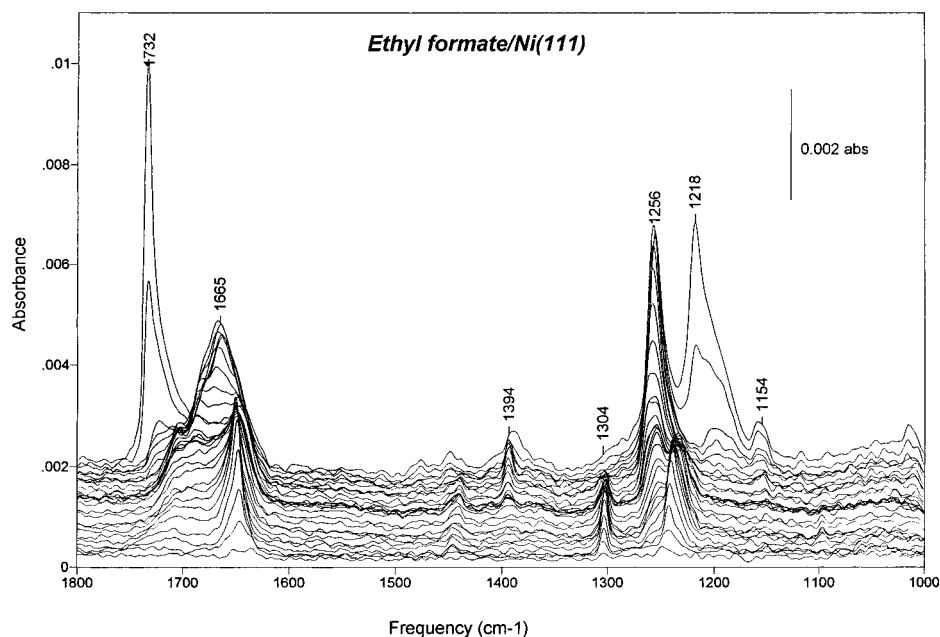


Figure 1. Rapid acquisition RAIRS spectra recorded sequentially during ethyl formate exposure to Ni(111) at 1×10^{-8} Torr with the sample held at 105 K. The topmost spectra display absorption bands characteristic of condensed or multilayer ethyl formate.

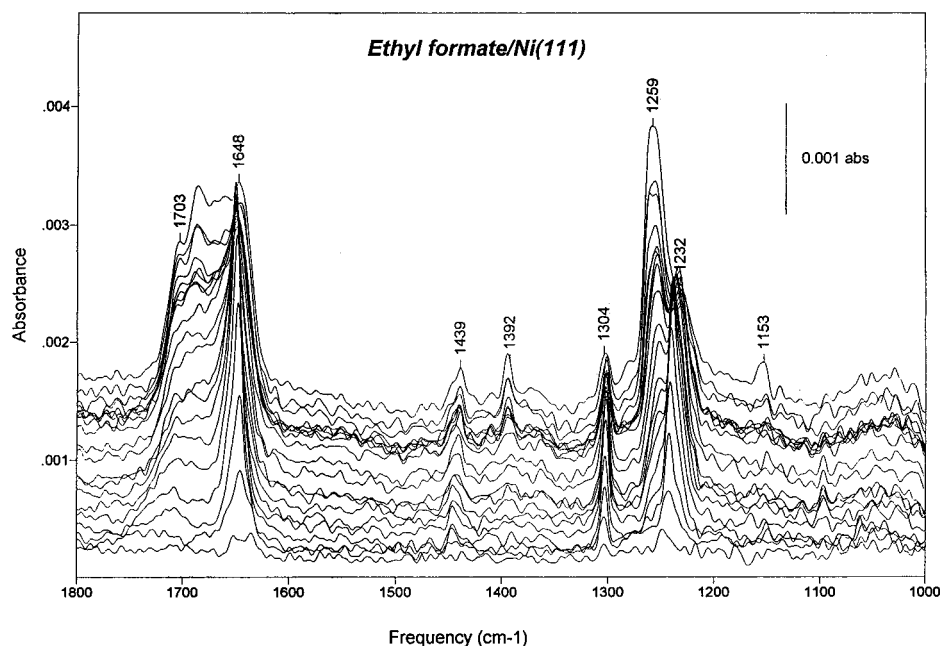


Figure 2. This figure shows more detail on the zero to two-thirds monolayer coverage spectra displayed in the previous figure.

such conformers may be varied is through complexation to a Lewis acid, particularly one containing bulky groups.^{16–18} Still another way is through the formation of a chemisorption layer, as has been shown by Zahidi et al^{3,4} for methyl and ethyl formate on Ni(111).

Experimental Section

The experiments were performed in a two-level ultrahigh-vacuum system equipped for XPS, TPD, and RAIRS measurements. The Ni(111) crystal was cleaned by repeated cycles of sputtering, hydrogen treatment, and annealing to 950 K. The surface cleanliness was verified using XPS measurements. Ethyl formate was further purified by carrying out several freeze–thaw cycles in the gas handling line. Details of the RAIRS instrument, experiment, and optical path are given elsewhere.¹⁹

Spectra in the CH stretching region were recorded using an InSb detector, and spectra in the midfrequency region were recorded using an MCT detector. Two types of RAIRS measurements were performed, namely rapid measurements made during gas exposures and slower measurements made after specific exposures. Rapid scan measurements were recorded sequentially (Figures 1 and 2) at a rate of one spectrum every 30 s by taking the ratio of 100 scans during gas exposure to 800 scans of the clean surface. Thus for example, up to 29 spectra were recorded during exposure at a background (uncorrected) pressure of 1×10^{-8} Torr prior to the emergence of absorption bands characteristic of multilayer ethyl formate. The CH stretching region spectra displayed in Figure 3 were obtained by taking the ratio of 800 sample scans to 800 background scans. Measurements using the MCT detector did not yield an adequate signal-to-noise ratio in the CH stretching region. XPS calibration

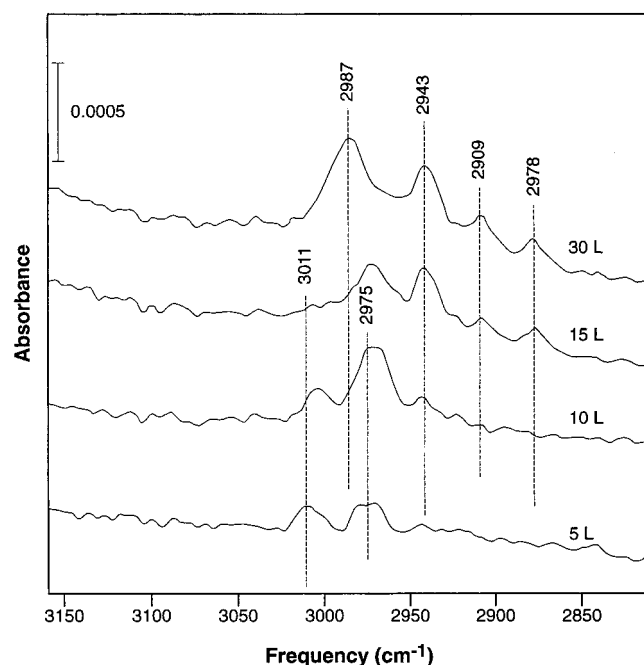


Figure 3. CH stretching region RAIRS spectra for increasing coverages of ethyl formate on Ni(111) at 105 K.

measurements show that the surface coverage changes linearly with exposure.^{3,4}

Results

The RAIRS spectra shown in Figure 1 give an overall view of the changes in relative band intensities which occur as the surface coverage of ethyl formate is increased on clean Ni(111) up to, and above, the monolayer level. Figure 2 is used to provide extra detail on spectra acquired for the same sequence of exposures up to approximately two-thirds of the monolayer coverage. The onset of multilayer formation is clearly indicated in Figure 1 by the emergence of the $\nu_{as}(\text{C}-\text{O}-\text{C})$ band at 1218 cm^{-1} and the $\nu(\text{C}=\text{O})$ band at 1732 cm^{-1} . Both of these band frequencies are characteristic of free ethyl formate.¹² A complex set of changes occurs prior to the establishment of monolayer coverage. In particular, the intensities of the bands at 1394 and 1304 cm^{-1} display opposing coverage dependences. The band at 1304 cm^{-1} grows in as the coverage is increased from zero and then fades out as monolayer coverage is approached. In contrast, the band at 1394 cm^{-1} only begins to grow in as the intensity of the 1304 cm^{-1} band begins to decrease. The CH stretching region spectra (Figure 3) show a peak at 3011 cm^{-1} , which displays the same coverage dependence as the band at 1304 cm^{-1} , and a band at 2943 cm^{-1} , which displays a similar coverage dependence as the band at 1394 cm^{-1} . Furthermore, the $\nu_{as}(\text{C}-\text{O}-\text{C})$ band appears at 1232 cm^{-1} at low coverages and is then replaced by a band at 1259 cm^{-1} at higher coverages. Likewise, the $\nu(\text{C}=\text{O})$ band appears at 1648 at low coverages and is then replaced by a band at 1665 cm^{-1} at monolayer coverage. The bands at 1232 and 1648 cm^{-1} may be attributed by the species giving rise to the bands at 1304 and 3011 cm^{-1} . In contrast the full monolayer coverage species displays characteristic bands at 1256, 1394, 1665, and 2943 cm^{-1} . Hence, the low and full coverage spectra arise from two distinct species. It should also be noted that the respective $\nu_{as}(\text{C}-\text{O}-\text{C})$ and $\nu(\text{C}=\text{O})$ band envelopes are narrowest at full coverage and at very low coverages. We attribute this to the presence of single well defined adsorption states at both low coverage and full monolayer coverage. In contrast the complexity of the

$\nu(\text{C}=\text{O})$ region at intermediate exposures suggests that there are a mixture of species on the surface. In particular, the spectra shown in Figure 2 clearly display a $\nu(\text{C}=\text{O})$ feature at $\sim 1687 \text{ cm}^{-1}$, in addition to the band at 1648 cm^{-1} .

Considerable care is needed in making assignments of the observed CH stretching region bands displayed in Figure 3. Two vibrational conformational analyses of free ethyl formate were recently reported by van der Veken et al.,^{12,13} and these authors pointed out that the IR spectrum contains many weak and very weak intensities making an assignment of band positions difficult. A few of the vibrational assignments of the first paper¹² were revised in the second paper¹³ in light of 6-31G** level ab initio calculated IR intensities. The assignments given in ref 13 and summarized in Table 1 permit a preliminary analysis of the $\nu(\text{CH})$ stretching data. First, the band observed at 3011 cm^{-1} in the low-coverage spectra may be uniquely assigned to the CH_2 asymmetric stretching vibration of the *s-cis,gauche* conformation. Features at 3010 and 3012 cm^{-1} in the IR and Raman gas-phase spectra¹² are assigned to this mode of *s-cis,gauche* ethyl formate, in agreement with the calculated¹³ vibrational frequency of 3011 cm^{-1} . Second, all the absorption bands above 2960 cm^{-1} may be attributed to asymmetric CH_2 or CH_3 vibrations. Spectrum 3c shows that four CH stretching bands are observed at approximately monolayer coverage. The highest frequency vibration, at 2975 cm^{-1} , is within the frequency range for asymmetric vibrations of planar ethyl formate. Thus, it must be assigned to the in-plane asymmetric CH_3 stretching vibration. The three lower frequency bands are, without initially specifying which band is which, then due to the CH stretching vibration and the symmetric CH_2 and CH_3 stretching vibrations.

Discussion

We first consider the 1800–1000 cm^{-1} region spectra displayed in Figures 1 and 2. The coverage dependence of the bands at 1304 and 1394 cm^{-1} may be interpreted in terms of preferential adsorption in the *c-cis,gauche* conformation at low coverages followed by complete rotamerization to either a *c-cis,trans* or a *s-trans,trans* conformation at full monolayer coverage.^{3,4} The dominant presence of *s-cis,gauche* ethyl formate at low coverages is directly indicated by the frequency and the RAIRS activity of the CH_2 twisting mode. The observed frequency, 1304 cm^{-1} , is sufficiently characteristic to fingerprint the *s-cis,gauche* conformation, since this mode appears at 1306 and 1278 cm^{-1} in gas-phase spectra of the *s-cis,gauche* and *s-cis,trans* conformations, respectively. Its RAIRS activity is also a very strong proof for the *s-cis,gauche* conformer. Since ethyl formate adsorbs on Ni(111) with its HCOO plane perpendicular to the surface,¹⁹ the observation of the CH_2 twisting mode, which belongs to the a'' representation in C_s point group symmetry, implies the presence of the lower symmetry *s-cis,gauche* conformation. Conversely, its absence at monolayer coverage is consistent with complete rotamerization to a planar, C_s symmetry, conformation. This rotamerization is also reflected in the opposing coverage dependent behavior of the bands at 1445 and 1394 cm^{-1} . The latter bands may be assigned, with a reasonable degree of certainty, to asymmetric and symmetric CH_3 deformation vibrations, respectively. The activity of the CH_3 symmetric deformation mode at monolayer coverage suggests a surface geometry in which the vector described by the ethyl CC bond has a significant component normal to the surface. Conversely, its absence at low coverages may be attributed to the ethyl CC bond lying roughly parallel to the surface in the adsorbed *s-cis,gauche* conformation.

The tilt of the ethyl CC bond with respect to the surface normal is, however, not known since the angle that the carbonyl

TABLE 1: Experimental^{a,b} Vibrational Frequencies (cm⁻¹) for Gas-Phase Ethyl Formate (Z)-Conformers

mode	<i>s-cis,trans</i>	<i>s-cis,gauche</i>	mode	<i>s-cis,trans</i>	<i>s-cis,gauche</i>
$\nu_{as}(\text{CH}_3)$	2998	2985	$\delta_{as}(\text{CH}_3)$	1453	1462
$\nu_{as}(\text{CH}_3)$	2986	2974	$\delta_{as}(\text{CH}_3)$	1441	1453
$\nu_{as}(\text{CH}_2)$	2972	3012	$w(\text{CH}_2), \delta_s(\text{CH}_3)$	1404	1404
$\nu_s(\text{CH}_2)$	2937	2952	$\rho(\text{H}-\text{C}=\text{O})$	1392	1392
$\nu(\text{HC})$	2930	2930	$\delta(\text{CH}_3), w(\text{CH}_2)$	1366	1370
$\nu_s(\text{CH}_3)$	2903	2903	$\text{tw}(\text{CH}_2)$	1278	1308
$\nu(\text{C}=\text{O})$	1750	1750	$\nu_{as}(\text{C}-\text{O}-\text{C})$	1191	1191
$\delta(\text{CH}_2)$	1485	1473			

^a Reference 12. ^b Reference 13.

bond makes with respect to the surface normal is also not known. Nevertheless, some idea as to the range of plausible Ni–O–C angles may be gained by considering structural data for carbonyl–Lewis acid complexes, since carbonyl chemisorption layers and Ni(111) and sterically hindered Lewis acid–formate adducts display some common features. For example, the vibrational shifts introduced when molecules such as methyl formate, ethyl formate, and methyl acetate bond to Ni(111) are very similar to those observed for complexation of these molecules to Lewis acids, implying a similar carbonyl lone pair dative bonding mechanism in both cases.^{19,20,21} Furthermore, steric factors²² are also clearly important in close packed chemisorption layers. Solid-state crystallographic studies show that the carbonyl lone pair bonding to Lewis acids need not necessarily result in an M–O–C angle of approximately 120°, as steric repulsion can easily lead to significant modifications of this angle.²² For example, LePage and Wiberg²³ conclude, on the basis of a theoretical study, that steric repulsion in carbonyl compound–Lewis acid donor–acceptor complexes may be relieved by opening the M–O–C angle at small energetic cost. Similarly, calculations by Brandachell and Olivia²⁴ predict that a formaldehyde/TiCl₄ complex with a Ti–O–C angle of 172° is only 1.7 kcal/mol less stable than one with a Ti–O–C angle of 146°. Experimental data supports these predictions since, for example, Ti–O–C angles of 152 and 169°, respectively, are observed²² for ethyl acetate²⁵ and ethyl anisate²⁶ bonded to octahedrally coordinated TiCl₄ dimers. Since considerable steric repulsion can develop in closely packed adlayers,²⁷ it appears reasonable to assume that the Ni–O–C angle will vary as a function of the surface coverage and that the high coverage structure will be oriented so as to give a small molecular footprint on the surface. The most compact surface structures of *s-cis,trans* and *s-trans,trans* ethyl formate, as illustrated in Chart 1, present Ni–O–C bond angles of approximately 125 (35 with respect to the surface plane) and 158°, respectively, and are thus plausible structures.

The CH stretching region spectra displayed in Figure 3 provide another perspective for evaluating conformational changes in the ethyl formate adlayer. The low coverage conformation may be unambiguously identified as *s-cis,gauche* on the basis of the RAIRS band at 3011 cm⁻¹, since Table 1 shows that the latter band may only be attributed to the CH₂ asymmetric stretching vibration of the *s-cis,gauche* conformation. It is, in any case, an out of plane vibration (a'' in C_s symmetry) and would not be RAIRS active for adsorbed perpendicularly oriented planar structures. Furthermore, as may be seen by comparing Figures 1 and 3, the coverage dependence of this band is the same as that of the band at 1304 cm⁻¹. Both bands may be attributed, uniquely, to normal modes of the adsorbed *s-cis,gauche* conformer, and both are out of plane vibrations.^{11,13} Hence, the $\nu(\text{CH})$ data confirm that ethyl formate preferentially adopts the *c-cis,gauche* conformation on Ni(111) at low coverages and that rotamerization to yield a planar

structure occurs, progressively, as the coverage is increased to the monolayer level.

Although a definitive conclusion cannot be reached as to whether the full monolayer geometry is *s-cis,trans* or *s-trans,trans*, the CH region stretching band frequencies are more consistent with the *s-trans,trans* conformation. The calculated vibrational data given in ref 12 predict that the three lowest frequency in-plane $\nu(\text{CH})$ bands for the *s-trans,trans* conformation appear at least 20 cm⁻¹ below the respective frequencies for the (Z) conformations. The three lowest frequency bands observed at monolayer coverage also display frequencies lower than those listed in Table 1 for the (Z) conformers, thereby suggesting the *s-trans,trans* structure as the conformation in the close packed monolayer. The theoretical work¹² also predicts that the third lowest frequency in-plane $\nu(\text{CH})$ band for the *s-trans,trans* conformation is due to the symmetric CH₃ stretching vibration, whereas it is the lowest frequency vibration for the (Z) conformers. A comparison of Figures 1 and 3 shows that the symmetric CH₃ deformation band (at 1394 cm⁻¹) displays the same coverage dependence as the third lowest frequency $\nu(\text{CH})$ band (at 2943 cm⁻¹). The latter two bands first appear as the those specifically associated with the *s-cis,gauche* conformation begin to fade out and then grow in intensity until monolayer coverage is reached. This correlation suggests the assignment of the bands at 2943 and 1394 cm⁻¹ to the symmetric CH₃ stretching and symmetric CH₃ deformation modes, respectively, of adsorbed *s-trans,trans* ethyl formate.

The $\nu_{as}(\text{C}-\text{O}-\text{C})$ and $\nu(\text{C}=\text{O})$ band frequencies have proven very useful for differentiating (E) and (Z) conformations of free formic acid esters such as cyanomethyl formate,²⁸ methyl formate,²⁹ and chloromethyl formate.³⁰ In each case, the *s-trans,trans* structure displays a blue-shifted $\nu(\text{C}=\text{O})$ band and a red-shifted $\nu_{as}(\text{C}-\text{O}-\text{C})$ band with respect to the *s-cis,trans* conformation. The observed blue-shifts of the $\nu(\text{C}=\text{O})$ band are in the range 32–38 cm⁻¹, and the red-shifts of the $\nu_{as}(\text{C}-\text{O}-\text{C})$ band for cyanomethyl and chloromethyl formate are 32 and 29 cm⁻¹, respectively. There are no experimental data available for free ethyl formate; however calculated spectra³¹ display a blueshift of 61 cm⁻¹ and a red shift of 32 cm⁻¹, for the $\nu(\text{C}=\text{O})$ and $\nu_{as}(\text{C}-\text{O}-\text{C})$ frequencies, respectively, on rotamerization from *s-cis,gauche* to *s-trans,trans*. Figures 1 and 2 show that the $\nu(\text{C}=\text{O})$ frequency of chemisorbed ethyl formate is blue shifted on going from the low coverage (*s-cis,gauche*) adsorbed structure to the full monolayer structure, as might be expected for rotamerization to a *s-trans,trans* conformation. However, the $\nu_{as}(\text{C}-\text{O}-\text{C})$ frequency is also blue shifted in contrast to what is expected for such a transformation. A possible explanation for the latter discrepancy may arise from the fact that the $\nu_{as}(\text{C}-\text{O}-\text{C})$ mode of ethyl formate is highly mixed,¹¹ coupled to the fact that its frequency is very sensitive to chemisorption bonding.¹⁹ Hence, we place more emphasis on the behavior of the relatively pure $\nu(\text{C}=\text{O})$ mode. Since only a very weak shift ($\sim +5$ cm⁻¹) of the carbonyl stretching

frequency is predicted for *s-cis,gauche* to *s-cis,trans* isomeration, the observed shift of 17 cm^{-1} (1648 to 1665) observed at close to monolayer coverage (highest coverage spectrum in Figure 2) points toward isomeration to the *s-trans,trans* structure. However, this conclusion is far from definitive since coverage-dependent changes in the Ni–O–C bond angle, the attendant changes in the chemisorption interaction, and changes in the extent of CO bond dipole–dipole coupling would also contribute to any observed shifts in the $\nu(\text{C}=\text{O})$ band frequency. Hence, the bulk of the proof for a full coverage *s-trans,trans* structure must rest with the correlation between the CH_3 group vibrations at 2943 and 1394 cm^{-1} . The CH_3 group vibrations are in any case the most reliable indicators since the CH_3 group is the part of the molecule the least perturbed by the chemisorption interaction.

Coverage-dependent rotamerization may be rationalized in terms of varying lateral interactions, and different molecule surface interactions, as the coverage of ethyl formate in the chemisorption layer is progressively increased. The dominant chemisorption interaction is the through the carbonyl lone pair.¹⁹ This interaction holds the molecule on the surface at all coverages. Decomposition of ethyl formate on Ni(111) competes with desorption;¹⁹ however, molecular desorption at full monolayer coverage occurs at 140 K indicating a adsorption strength of at least $8\text{--}9\text{ kcal mol}^{-1}$. The predominance of the *s-cis,gauche* conformation at low coverage is most likely due to the fact that it is the geometry for which the molecule makes maximum contact with the surface. In addition to the carbonyl lone pair interaction, this geometry permits the noncovalent bonding of the ethyl group to the surface. As a result the molecular footprint of the *s-cis,gauche* structure is relatively large. In contrast, the full coverage *s-trans,trans* structure would have a smaller molecular footprint and yet still permit the dominant carbonyl lone pair–nickel interaction. The *c-cis,trans* and *s-trans,trans* structures differ mainly in terms of the absolute values and components normal to the surface of their molecular dipole moments. Hence, dipole–dipole or dipole–image dipole interactions will play a complex role in determining which adsorbed structure is the most stable.

Conclusions

RAIRS measurements show that surface coverage dependent conformational change occurs for ethyl formate on Ni(111) at 105 K. The low-coverage conformation is *s-cis,gauche*. This conformation permits a noncovalent interaction of the ethyl group with the surface in addition to the carbonyl lone pair chemisorption bond formation. A comparison of the CH stretching region RAIRS data with calculated vibrational frequencies for ethyl formate conformers suggests that the full coverage conformation is most likely *s-trans,trans*. The rotamerization from *s-cis,gauche* to *s-trans,trans* may be attributed to a balance of varying lateral interactions, and varying molecule–metal interactions, within the progressively more closely packed adlayer.

Acknowledgment. We gratefully acknowledge financial assistance from NSERC (Research Grant) and FCAR (Équipe et Centre de Recherche (CERPIC)). M.C. acknowledges the receipt of an NSERC graduate scholarship. The machining assistance of André Bouffard is gratefully noted.

References and Notes

- (1) Pertsin, A. J.; Grunze, M.; Garbuzova, I. A. *J. Phys. Chem. B* **1998**, *102*, 4919.
- (2) (a) Baiker, A. *J. Mol. Catal. A* **1997**, *115*, 473. (b) Blaser, H.-U.; Jalett H.-P.; Muller, M.; Studer, M. *Catalysis Today* **1997**, *37*, 441.
- (3) Zahidi, E.; Castonguay, M.; McBreen, P. H. *Chem. Phys. Lett.* **1995**, *236*, 122.
- (4) Zahidi, E.; Castonguay, M.; McBreen, P. H. *J. Phys. Chem.* **1995**, *99*, 17906.
- (5) Udval, P.; MacKerell, A. D., Jr. *Surf. Sci.* **1997**, *393*, 141.
- (6) George, W. O.; Hassid, D. V.; Maddams, W. F. *J. Chem. Soc., Perkin 2* **1978**, 1798.
- (7) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.
- (8) Riveros, J. M.; Wilson, E. B. *J. Chem. Phys.* **1967**, *46*, 4605.
- (9) Tabuchi, D. *J. Chem. Phys.* **1958**, *28*, 1014.
- (10) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.
- (11) Charles, S. W.; Jones, G. I. L.; Owen, N. L.; Cyvin, S. J.; Cyvin, B. N. *J. Mol. Struct.* **1973**, *16*, 225.
- (12) Maes, I. I.; Herrebout, W. A.; van der Veken, B. J. *J. Raman Spectrosc.* **1994**, *25*, 679.
- (13) Peng, Z.; Shlykov, S.; Van Alsenoy, C.; Geise, H. J.; Van der Veken, B. *J. Phys. Chem.* **1995**, *99*, 10201.
- (14) Wiberg, K. B.; Wong, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 1078.
- (15) Pawar, D. M.; Khalil, A. A.; Hooks, D. R.; Collins, K.; Elliott, T.; Stafford, J.; Smith, L.; Noe, E. A. *J. Am. Chem. Soc.* **1998**, *120*, 2108.
- (16) Lewis, F. D.; Quillen, S. L.; Hale, P. H.; Oxman, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1263.
- (17) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.
- (18) Loncharich, R. J.; Schartz, T. R.; Houk, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 14.
- (19) Zahidi, E.; Castonguay, M.; McBreen, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 5847.
- (20) Anton, A. B.; Avery, N. R.; Toby, B. H.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 684.
- (21) Taillandier, M.; Liquier, J.; Taillandier, E. *J. Mol. Struct.* **1968**, *2*, 437.
- (22) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.
- (23) LePage, T. J.; Wong, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.
- (24) Branchadell, V.; Olivia, A. *J. Am. Chem. Soc.* **1992**, *114*, 4357.
- (25) Brun, L. *Acta Crystallogr.* **1966**, *20*, 739.
- (26) Bassi, I. W.; Calcaterra, M.; Intrito, R. *J. Organomet. Chem.* **1977**, *127*, 305.
- (27) Rösch, N.; Fox, Th.; Netzer, F. P.; Ramsey, M. G.; Steinmüller, D. *J. Chem. Phys.* **1991**, *94*, 3276.
- (28) Dahlqvist, M.; Hotokka, M.; Räsänen, M. *J. Phys. Chem.* **1997**, *101*, 1260.
- (29) Muller, R. P.; Hollenstein, H.; Huber, R. J. *J. Mol. Spectrosc.* **1983**, *100*, 95.
- (30) Räsänen, M.; Kunttu, H.; Murto, J.; Dahlqvist, M. *J. Mol. Struct.* **1987**, *159*, 65.
- (31) Reference 12 reports calculated spectra (4-21G level) for all four conformations of ethyl formate. The calculated $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ frequencies are 1209, 1210, and 1178 cm^{-1} for the *s-cis,gauche*, *s-cis,trans* and *s-trans,trans* conformations, respectively. The respective $\nu(\text{C}=\text{O})$ frequencies are 1756, 1761, and 1822 cm^{-1} .