

Adsorption and Reaction of NO on Cu(100): An Infrared Reflection Absorption Spectroscopic Study at 25 K

C. M. Kim,[†] C.-W. Yi, and D. W. Goodman*

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

Received: January 18, 2002; In Final Form: May 3, 2002

The adsorption of nitric oxide (NO) on a Cu(100) surface at 25 K has been studied using infrared reflection absorption spectroscopy (IRAS). Initially, NO adsorbs at the bridge site; however, with an increase in coverage, dimerization of NO occurs. Further dosing of NO at 25 K produces a multilayer of the NO dimer. Annealing this dimer multilayer to 40 K causes a change in the alignment of the dimers in the multilayer with respect to the Cu(100) surface. Heating to 55 K leads to reorientation of the dimer molecules in the multilayer such that the N–N axis becomes perpendicular to the surface; at 60 K the multilayer NO dimers desorb. Formation of N₂O was observed upon heating the surface above 60 K.

1. Introduction

Adsorption at 80 K or higher is frequently adequate for studying molecular chemisorption on many metal surfaces. However, for relatively weakly bound species on certain surfaces, e.g., metal oxides, studies below 80 K may be required to address the details of molecule–surface interactions. Temperatures below 80 K also facilitate the investigation of molecule–molecule interactions in surface multilayers.

In the present study, the adsorption of nitric oxide on Cu(100) at ca. 25 K has been investigated using infrared reflection absorption spectroscopy (IRAS). Previous studies have shown that reaction of NO on Cu(100) takes place at temperatures as low as 90 K.^{1–3} Cooling the substrate to temperatures below 90 K then is necessary to investigate molecular NO adsorption on Cu(100). Here we report a study of the NO multilayer formation on Cu(100) at ~25 K, the change in the multilayer structure in the temperature range 40–60 K, the subsequent formation of chemisorbed NO, and finally NO dissociation.

The interaction of NO with metal and metal oxide surfaces has been the topic of numerous surface science studies. Because NO has an unpaired electron in the $2\pi^*$ orbital, chemisorption of NO on metal surfaces can be rather complicated compared to that of CO. It has been found that NO forms several reaction products on various metal surfaces even at liquid-nitrogen temperature in ultrahigh vacuum (UHV). The extensive studies of the interaction of NO with metal surfaces have been reviewed recently.⁴

The reaction of NO with Cu single-crystal surfaces in UHV has been addressed by several research groups. Johnson et al. investigated the adsorption of NO on Cu(100) and Cu(111) using X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED).¹ This group reported “bent” and “linear” NO species on copper surfaces at 80 K. Bent NO dissociated at 80 K while the linear species desorbed above 170 K. These authors also reported the formation of N₂O and that Cu(100) was more active than

Cu(111) for NO dissociation. Using electron energy loss spectroscopy (EELS), Wendelken concluded that N₂O was formed at 85 K with relatively low exposures of Cu(100) to NO.² N₂O on Cu(111) was also observed to form from NO using HREELS and temperature desorption spectroscopy (TDS),⁵ in agreement with observations on Cu particles supported on Al₂O₃.⁶ King and co-workers observed that NO adsorbed molecularly upon initial adsorption on Cu(110) at 40 K using IRAS.⁷ A dimeric (NO)₂ species formed with further exposure, followed by the formation of a (NO)₂ multilayer below 60 K. These authors also reported that N₂O was formed from the NO dimer species. A synchrotron IRAS study indicated the formation of a Cu–ON₂ and a NO dimeric species on Cu(111).⁸ A secondary ion mass spectrometric (SIMS) study of NO-adsorption on Cu(100) reported molecular NO along with reaction products including O, N, NO₂, NO₃, and N₂O₄ at 110 K.³

In the present study of NO adsorption on Cu(100), we have concentrated on the formation of the NO dimer and the subsequent formation of a dimer multilayer. We have also studied the change in the molecular orientation of the dimer in the multilayer upon annealing.

2. Experimental Section

The experiments were carried out in an UHV chamber equipped with IRAS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a quadrupole mass spectrometer.

The IRAS spectra were obtained using a Matteson Cygnus 100 spectrometer with a liquid-nitrogen-cooled, mercury cadmium telluride (MCT) detector. All IRAS were acquired with a resolution of 4 cm⁻¹, and 800–1600 scans were taken depending on the signal-to-noise ratio. The instrumentation and data acquisition for IRAS have been described in detail.⁹ The sample was mounted on a modified heating and cooling sample stage (Vacuum Generators) attached to a continuous flow liquid helium cryostat. The sample could be cooled to 21 K and heated to 1100 K. The temperature was measured using a K-type thermocouple that was calibrated below 80 K using a thermocouple reference junction at liquid nitrogen temperature (77 K). The calibrated temperature was compared to the desorption temperature for multilayer CO (30 K).^{10–11}

* Author to whom correspondence should be addressed. Fax: 979-845-6822. E-mail: goodman@mail.chem.tamu.edu.

[†] On leave from Department of Chemistry, Kyungpook National University, Taegu, 702-701, Korea.

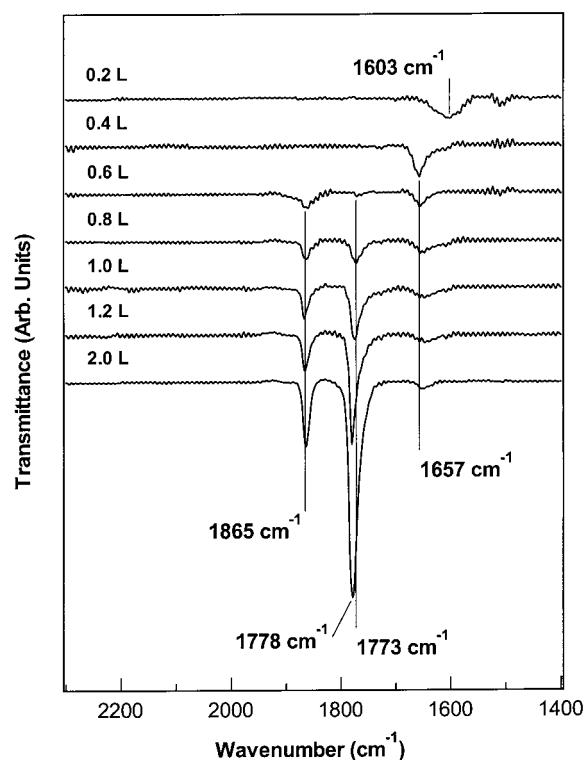


Figure 1. IRAS of NO adsorbed on Cu(100) at the indicated NO exposure. The adsorption temperature was 25–28 K.

The Cu(100) single-crystal sample was cleaned by repeated cycles of argon ion sputtering at 300 K and annealing at 750 K. The cleanliness and ordering of the sample surface was checked by AES and LEED. NO was dosed using a precision leak valve. The NO purity was determined via its gas phase mass spectrum and the IR spectrum of the condensed gas at 25 K. The only impurity was a trace amount of N₂O.

3. Results and Discussion

Figure 1 shows the change in the IRAS as a function of exposure of NO on Cu(100) at 25 K. At low coverages of NO, a broad feature at 1603 cm⁻¹ is apparent. This band shifts to 1657 cm⁻¹ upon further NO exposure. At a NO exposure of 0.6 L, a new band appears at 1865 cm⁻¹ and a second feature appears at ca. 1773 cm⁻¹. The 1773 cm⁻¹ band shifts to 1778 cm⁻¹ at NO exposures greater than 1 L.

The stretching frequency of NO adsorbed on metal surfaces ranges from 1200 to 1900 cm⁻¹ depending upon the adsorption geometry, i.e., 3-fold linear, 2-fold bent, 2-fold linear, bent atop, and linear atop. Bridge-bonded NO has been observed on Cu(100) and Cu(111) within the frequency range 1532–1650 cm⁻¹.^{2,5} King and co-workers reported that NO initially adsorbs on Cu(110) in a bridging site with a bent configuration, changing to an upright configuration as the coverage is increased.⁷ The bands at 1603 and 1657 cm⁻¹ can be assigned to the N–O stretch of a bridge-bonded NO species. Whether this bridge-bonded NO is bent or upright cannot be assessed since the NO bending mode region (~880 cm⁻¹) was not assessable in the present experiments.

Two bands at 1865 and 1773–1778 cm⁻¹ can be assigned to symmetric (ν_1) and asymmetric (ν_5) stretching features of NO dimers. Formation of the dimer was confirmed using ¹⁵N-labeled NO. Figure 2 shows the IR spectra of ¹⁴NO, ¹⁵NO, and a ¹⁴NO–¹⁵NO mixture. After dosing ¹⁵NO, the bands at 1865 and 1775 cm⁻¹ for ¹⁴NO shifted to 1831 and 1744 cm⁻¹, respec-

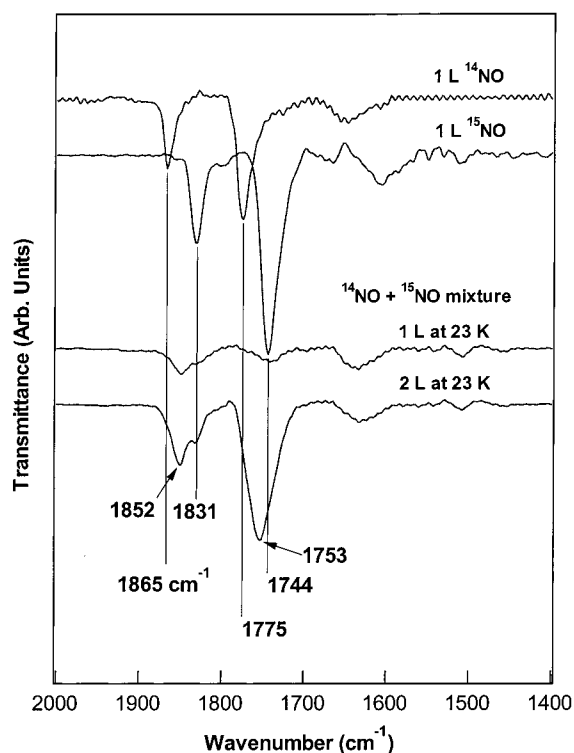


Figure 2. Comparison of ¹⁴NO, ¹⁵NO, and a mixture of ¹⁴NO and ¹⁵NO adsorbed onto Cu(100). The bands at 1865 and 1753 cm⁻¹ clearly indicate the formation of the O¹⁴N–¹⁵NO dimer.

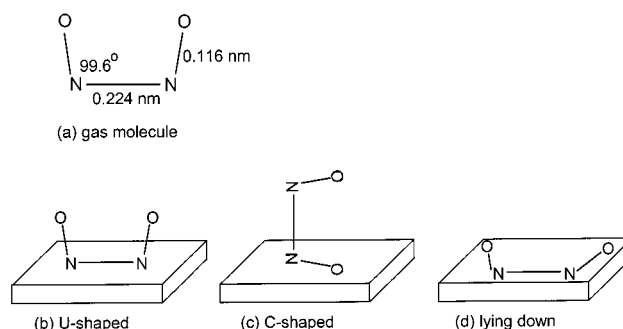


Figure 3. (a) Structure of the gas-phase NO dimer.¹⁶ (b)–(d) Possible bonding orientations of the NO dimer on the surface. In IRAS, the ν_1 mode is active [see (b)] and the ν_5 mode is active [see (c)]. The lying-down configuration of the dimer [see (d)] is not detectable by IRAS.

tively. New bands appeared at 1852 and 1753 cm⁻¹ following dosing of a mixture of ¹⁴NO–¹⁵NO on Cu(100). These features correspond to the symmetric and asymmetric stretching bands of the O¹⁴N–¹⁵NO dimer. The intensities of the mixed dimer were very near the statistical population expected following exposure to a 3:4 mixture of ¹⁴NO–¹⁵NO.

Because of an unpaired electron in the π^* orbital, the NO dimer is produced from monomers without activation energy.^{12–16} Several isomers of NO dimers including *cis*-ONNO, *trans*-ONNO, *cis*-ONON, and *trans*-ONON have been identified. It is now generally accepted that a *cis*-ONNO with a planar configuration is the most stable isomer. The reported structure of the gas-phase NO dimer is shown in Figure 3. Dimeric NO is formed in the gas phase at low temperatures¹² as well as in the condensed phase.¹⁷ Formation of (NO)₂ also has been reported to form upon condensation of NO in an argon or nitrogen matrix^{18–20} and when adsorbed on solid surfaces including Cu(110),⁷ Cu(111),⁸ Pd(111),²¹ Ag(111),^{22,23} Al₂O₃,²⁴

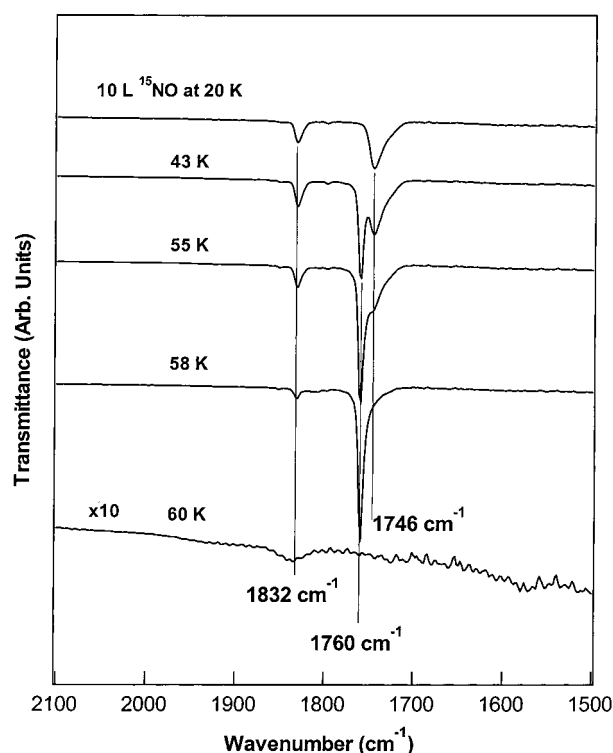


Figure 4. IRAS of a ^{15}NO -dimer multilayer on Cu(100) as a function of annealing temperature.

TABLE 1: Symmetric (ν_1) and Asymmetric (ν_5) Vibrational Frequencies of ON–NO

type of sample	symmetric (ν_1)	asymmetric (ν_5)	method	ref
on Cu(100)	1865	1773(chemisorbed) 1778(multilayer) 1788 (ordered multilayer)	IRAS	this work
gas	1860	1788	IR	12
solid	1862	1768, 1740(trans)	IR	27
solid	1866	1762	Raman	17
N_2 matrix	1870	1776, 1764(trans)	IR	20
Ar matrix	1863.4	1776.3	IR	19
on Pd(111)	-	1782(multilayer)	HREELS	21
on Ag(111)	1863	1788	IRAS	22
on Cu(110)	1850	1780	IRAS	7
on Cu(111)	1830	1780	IRAS	8

and graphite.^{25,26} The symmetric (ν_1) and asymmetric (ν_5) stretching frequencies of NO dimers are summarized in Table 1.

The orientation of the NO dimer on the surface can be determined using the surface selection rule of IRAS, i.e., only those vibrations whose dipole moments are perpendicular to the surface are detected. Figure 3 shows the possible orientations of an adsorbed NO dimer. In the monolayer regime, the intensity of the symmetric band is much greater than that of the asymmetric band, implying that $(\text{NO})_2$ is adsorbed with a “U-shaped” geometry with the N–N bond adsorbed parallel to the surface. The presence of the weak asymmetric band in the monolayer regime (0.6 L spectrum in Figure 1) implies that the second layer of NO is formed before the surface is completely covered with the first layer. It has been reported that the NO dimer is adsorbed on Ag(111) in an up-right (U-shaped) configuration with its molecular plane tilted by 30° relative to the surface normal based on IRAS²² and NEXAFS²³ data. As the coverage of $(\text{NO})_2$ is increased, the intensities of both the symmetric and asymmetric bands increase; however, the asymmetric stretching intensity is enhanced to a larger extent than the symmetric stretching intensity. Upon formation of the

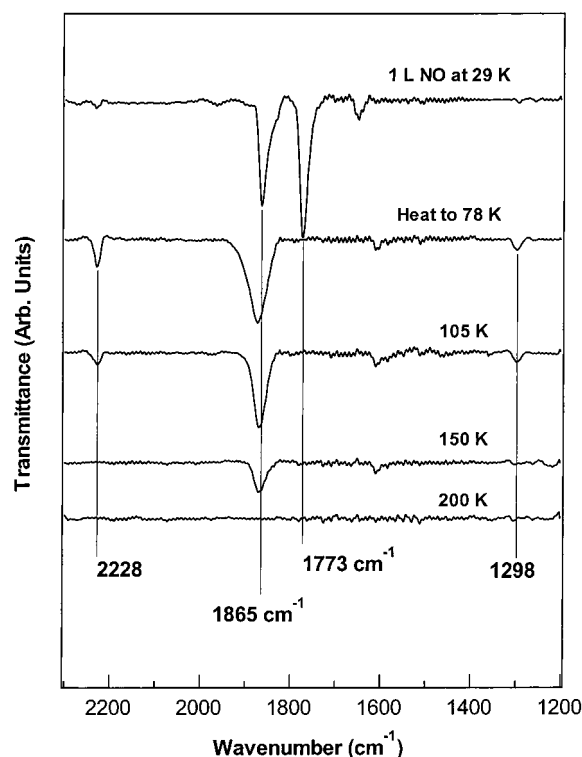
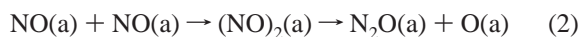


Figure 5. IRAS of NO on Cu(100) in the monolayer regime as a function of surface temperature.

multilayer, the intensity ratio of the symmetric and asymmetric bands is very close to that of gas phase and solid $(\text{NO})_2$,¹⁹ implying that the NO dimer is randomly oriented in the multilayer.

The reactivity of the NO dimer on Cu(100) was investigated as a function of temperature using IRAS. Figure 4 shows the change in the IRAS spectra of ^{15}NO multilayers on Cu(100) as the surface temperature is varied. At 43 K, a new feature appears at 1760 cm^{-1} . At 58 K, the band at 1746 cm^{-1} and the symmetric stretching band at 1832 cm^{-1} are greatly attenuated. For the ^{14}NO -dimer multilayer, the asymmetric stretching band shifts from 1778 to 1788 cm^{-1} upon annealing to 55 K (spectra not shown). However, the shift of the symmetric stretching band was negligible. Matrix isolation experiments have shown that the vibrational frequencies of $(\text{NO})_2$ are greatly affected by the size of the dimer clusters and the molecular interaction among dimers. It has been reported that the asymmetric mode is more perturbed by the dimer environment than the symmetric mode.¹⁹ It is noteworthy that the intensity of the asymmetric stretching band increases by a factor of 3 while the fwhm decreases by one-half as the peak shifts from 1746 to 1760 cm^{-1} . Desorption of NO was not observed until the surface temperature reached 60 K. This observation clearly demonstrates that the morphology of the multilayer NO dimer is changed within the temperature range of 40–60 K. Although we do not have detailed structural data, the morphology of $(\text{NO})_2$ multilayer can be deduced from the surface selection rule and the relative intensities of the symmetric (ν_1) and asymmetric stretching (ν_5) bands. The intensity of the ν_5 band of $(\text{NO})_2$ would be at its maximum when the molecule is oriented with the N–N bond perpendicular to the surface since the dipole is aligned with the N–N bond. In the case of the ν_1 band, the maximum intensity should occur when the N–O bond is aligned perpendicular to the surface. The significant increase of the ν_5 band intensity in our experiment implies that the NO dimer is aligned with the N–N bond perpendicular to the surface plane (“C-shaped” in Figure 3).

The reaction of NO in the monolayer regime as a function of the surface temperature is shown in Figure 5. The dosing temperature was 29 K and the spectra were acquired while maintaining the temperature indicated in the figure. Upon heating to 78 K, the bands at 2228 and 1296 cm^{-1} were clearly resolved. These bands were assigned to correspond to the N–N and N–O stretching modes of N_2O , respectively. Formation of N_2O from NO adsorbed on metal surfaces has been frequently reported.⁴ There are two possible mechanisms for the formation of N_2O from NO adsorbed on the surface.



That significant amounts of $(\text{NO})_2$ are present on the surface prior to the formation of N_2O suggests that N_2O is formed via the second mechanism. At 110 K, decomposition and desorption of N_2O takes place. At 200 K, the NO bands disappear.

4. Conclusion

The adsorption and reaction of nitric oxide adsorbed on Cu(100) at 25 K have been studied using IRAS. The results and main conclusions are as follows:

1. Bridge-bonded NO was formed at low coverage whereas $(\text{NO})_2$ dimers were formed as the coverage increased.
2. In a NO multilayer formed at 25 K, the NO dimer is randomly oriented. However, dimeric molecules rearrange upon annealing and are aligned with the N–N axis perpendicular to the surface at 55–58 K.
3. The NO dimer in the monolayer regime is a precursor to N_2O on the surface upon heating.

Acknowledgment. We gratefully acknowledge funding of this work by the Department of Energy, Office of Basic Energy

Sciences, Division of Chemical Sciences, and the Robert A. Welch Foundation.

References and Notes

- (1) Johnson, D. W.; Matloob, M. H.; Roberts, M. W. *J. Chem. Soc., Faraday Trans. 1* **1979**, 75, 2143.
- (2) Wendelken, J. F. *Appl. Surf. Sci.* **1982**, 11/12, 172.
- (3) Wee, A. T. S.; Lin, J.; Huan, A. C. H.; Loh, F. C.; Tan, K. L. *Surf. Sci.* **1994**, 304, 145.
- (4) Brown, W. A.; King, D. A. *J. Phys. Chem. B* **2000**, 104, 2578.
- (5) So, S. K.; Farnchy, R.; Ho, W. *J. Chem. Phys.* **1991**, 95, 1385.
- (6) Wu, M.-C.; Goodman, D. W. *J. Phys. Chem.* **1994**, 98, 9874.
- (7) Brown, W. A.; Sharma, R. K.; King, D. A.; Haq, S. *J. Phys. Chem.* **1996**, 100, 12559.
- (8) Dumas, P.; Suhren, M.; Chabal, Y. J.; Hirschmugl, C. J.; Williams, G. P. *Surf. Sci.* **1997**, 371, 200.
- (9) Leung, L.-W. H.; He, J.-W.; Goodman, D. W. *J. Chem. Phys.* **1990**, 93, 8378.
- (10) Cook, J. C.; McCash, E. M. *Surf. Sci.* **1996**, 359, L445.
- (11) Wichtendahl, R.; Rodrigurz-Rodrigo, M.; Härtel, U.; Kühlenbeck, H.; Freund, H.-J. *Phys. Status Solidi A* **1999**, 173, 93.
- (12) Dinerman, C. E.; Ewing, G. E. *J. Chem. Phys.* **1970**, 53, 626.
- (13) East, A. L. L.; McKellar, A. R. W.; Watson, J. K. G. *J. Chem. Phys.* **1998**, 109, 4378.
- (14) Menoux, V.; LeDucen, R.; Hauesler, C.; Deroche, J. C. *Can. J. Phys.* **1984**, 62, 322.
- (15) Fisher, I.; Strobel, A.; Staeker, J.; Niedner-Schatteburg, G.; Müller-Dethlefs, K.; Bondybey, V. E. *J. Chem. Phys.* **1992**, 96, 7171.
- (16) Kukolich, S. G. *J. Am. Chem. Soc.* **1982**, 104, 4715.
- (17) Nour, E. M.; Chen, L.-H.; Strube, M. M.; Laane, J. *J. Phys. Chem.* **1984**, 88, 756.
- (18) Canty, J. F.; Stone, E. G.; Bach, S. B. H.; Ball, D. W. *Chem. Phys.* **1997**, 216, 81.
- (19) Krim, L.; Lacome, N. *J. Phys. Chem. A* **1998**, 102, 2289.
- (20) Guillory, W. A.; Hunter, C. E. *J. Chem. Phys.* **1969**, 50, 3516.
- (21) Bertolo, M.; Jacobi, K. *Surf. Sci.* **1990**, 226, 207.
- (22) Brown, W. A.; Gardner, P.; King, D. A. *J. Phys. Chem.* **1995**, 99, 7065.
- (23) Brown, W. A.; Gardner, P.; Jigato, M. P.; King, D. A. *J. Chem. Phys.* **1995**, 102, 7277.
- (24) Paul, D. K.; Smith, B. W.; Marten, C. D.; Burchett, J. *J. Mol. Catal. A: Chem.* **2001**, 167, 67.
- (25) Suzanne, J.; Coulomb, J. P.; Bienfait, M.; Matecki, M.; Thomy, A.; Croset, B.; Marti, C. *Phys. Rev. Lett.* **1978**, 41, 760.
- (26) Nandhakumar, I. S.; Li, Z. Y.; Palmer, R. E.; Amos, R. *Surf. Sci.* **1995**, 329, 184.
- (27) Dolphin, D.; Wick, W. *Tabulation of Infrared Spectral Data*; Wiley: New York, 1977.