JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Strong Carbon-Surface Dative Bond Formation by *tert*-Butyl Isocyanide on the Ge(100)-2 × 1 Surface

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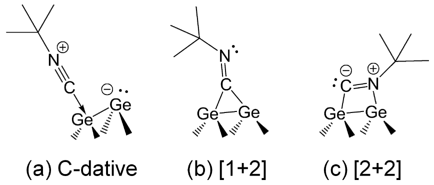
ABSTRACT: Carbon dative bond formation between an organic molecule and a semiconductor surface is reported here for the first time. Our studies show that the adsorption of *tert*-butyl isocyanide on the (100) surface of germanium, measured using Fourier transform infrared spectroscopy, temperature-programmed desorption, and density functional theory calculations, occurs via formation of a dative bond to the surface through the isocyanide carbon. The experimentally observed adsorption energy of 26.8 kcal/mol is the largest among any organic molecule dative bonded on the Ge(100)-2 × 1 surface studied to date. The dative-bonded adsorbate is characterized by a N≡C stretching frequency significantly blue-shifted from that of the free molecule. Moreover, the adsorbate N≡C vibrational frequency red-shifts back toward that of the free molecule upon increasing coverage. These spectroscopic effects are attributed to σ-donation of the isocyanide lone pair electrons to the surface.

Functionalization of semiconductor surfaces with organic molecules has been of much interest in recent years.[1−3] By creating interfaces between inorganic and organic functionalities, a plethora of future applications may become possible, from organic semiconductors to sensors to molecular scale patterning. The (100) surfaces of Ge and Si are of particular interest because of their importance in electronics technologies. These surfaces are highly reactive, with dimers formed in the 2 × 1 reconstruction that exhibit both double bond and zwitterionic character.[1,2] This surface property leads to analogies with organic chemistry such as dative bonding (σ-donation, coordinate covalent bonding) that occurs upon adsorption of many organic molecules at Si or Ge surfaces,[3,4] in which lone pair electrons of organic molecules are donated to the electron-deficient down atoms of the group 14 (100)-2 × 1 surface dimers.

Isocyanides (R−N≡C) are important in organic synthesis due to their unique structure containing a monocoordinated carbon.[5] The coordination chemistry and adsorption on metal surfaces of isocyanides have been thoroughly investigated.[6−9] Isocyanide adsorbates with σ-donating geometries on metal surfaces are known to form highly conductive n-type molecular junctions,[10−12] and such a bonding motif can be useful for modification of the band structure of semiconductor surfaces.[13,14] However, there are only few studies of isocyanide adsorption on semiconductor surfaces. Kugler et al. suggested that isocyanides yield [1 + 2] cycloaddition products on the Si(100)-2 × 1 surface,[15,16] in which the isocyanide carbon forms a three-membered ring with a Si dimer (analogous to Figure 1b), inferred from a reaction of isocyanide with disilene.[17] However, their theoretical methods could not account for the asymmetric tilt of the Si dimers,[18,19] which is important in describing the reactivity of group 14 semiconductor surfaces.[1,2] On the other hand, the lone pair electrons on the isocyanide C enable nucleophilic additions, which is a key step in many multicomponent reactions;[20] moreover, in reactions with Ge analogues of carbene and alkyne, isocyanides form linear C−Ge Lewis adducts.[21,22] On the Ge(100)-2 × 1 surface, isocyanides have been suspected as possible reaction byproducts of isothiocyanates,[23,24] but the adsorption chemistry of isocyanide on Ge(100)-2 × 1 has never been directly studied. Notably, all allowed structures of isocyanide adducts on Ge(100)-2 × 1 involve a C−Ge bond (Figure 1). Only a few reaction mechanisms that tether organic adsorbates through a direct carbon−germanium bond either via wet chemistry[25−27] or in vacuum[28,29] are known.



(a) C-dative (b) [1+2] (c) [2+2]

Figure 1. Possible adsorption configurations of TBIC on Ge(100)-2 × 1: (a) dative bond through isocyanide carbon, (b) [1 + 2] cycloaddition, and (c) [2 + 2] cycloaddition.

In this work, we investigate the adsorption of *tert*-butyl isocyanide (TBIC) on the Ge(100)-2 × 1 surface using Fourier transform infrared (FTIR) spectroscopy and temperature-programmed desorption (TPD) experiments coupled with density functional theory (DFT) calculations. We show that TBIC is bound to Ge(100)-2 × 1 by a dative bond through its isocyanide lone pair electrons (Figure 1a), providing a novel route to create a direct carbon-surface bond. The adsorption energy of this species is the strongest of any dative bonded organic adsorbates on Ge(100)-2 × 1 ever reported.

All experiments were conducted in a previously described ultrahigh vacuum (UHV) reaction chamber[30] with a base pressure of <1 × 10^{-10} Torr. The surface of a trapezoidal Ge(100) crystal (Harrick Scientific, 19 × 14 × 1 mm^3, 45° beveled edges) was cleaned via repeated Ar^+ sputtering and annealing, and the 2 × 1 reconstruction was confirmed by low energy electron diffraction (LEED). *tert*-Butyl isocyanide (98%, Alfa Aesar) was further purified by repeated freeze−pump−

Received: January 22, 2014
Published: April 11, 2014

thaw cycles. TBIC vapor was exposed to the Ge crystal through a variable leak valve. Surface exposures are reported in langmuirs (1 L = 10^{-6} Torr·s), which are not corrected for ionization gauge sensitivity. FTIR spectra were collected by a Nicolet 6700 FTIR spectrometer using an external HgCdTe detector in multiple internal reflection (MIR) geometry. Absorption by the CaF_2 viewports resulted in a low-frequency cutoff of ~1050 cm^{-1}. All FTIR spectra were manually corrected for baseline sloping. TPD experiments were conducted in the same reaction chamber using a method described previously.[31] Following TBIC exposure of 1 L at 300 K, the chamber pressure returned below 5×10^{-10} Torr within 10 min, at which time a linear surface temperature ramp of 1 K/s was initiated. The mass-to-charge ratios (m/e) of 27, 39, 41, 57, 68, and 83 were selected for monitoring based upon ionization spectra of TBIC in the literature.[32]

DFT calculations were carried out using the Gaussian 03 suite[33] with the B3LYP functional. $Ge_{15}H_{16}$ two-dimer and Ge_9H_{12} one-dimer clusters were used to model the Ge(100)-2 × 1 surface. The adsorbate molecules and the Ge dimer atoms were modeled with a 6-311++G(d,p) basis set, a LANL2DZ pseudopotential was used for subsurface Ge atoms, and the terminating H atoms were modeled with a 6-31G(d) basis set. In vibrational frequency calculations, the terminating hydrogen atoms were assigned a mass of 74.0 u to match the atomic mass of Ge. The calculated IR frequencies were scaled by a factor of 0.97.[34] Lorentzian line shapes with a fwhm of 10 cm^{-1} and relative calculated intensities were used to represent IR bands. The synchronous transit-guided quasi-Newton (STQN) method as implemented in Gaussian 03 was used to locate transition states,[35] which were subsequently confirmed as having a single imaginary vibrational mode along the reaction coordinate. Zero-point energy corrections were applied to all reported energies. The molecular orbitals were visualized using MOLEKEL[36] with an isovalue of 0.05.

Figure 2 shows FTIR spectra of TBIC adsorbed on Ge(100)-2 × 1. The N−C stretching frequency indicates the configuration of the isocyanide functionality.[7,8] Specifically, the feature near 2190 cm^{-1} in the chemisorption spectra can be assigned to the triple bonded N≡C stretching mode resulting from the C-dative bonded product. This assignment is confirmed by comparison with DFT-calculated IR spectra of possible product structures, among which only the C-dative structure has a $\nu(N{\equiv}C)$ mode above 2100 cm^{-1}. The other structures such as [1 + 2] and [2 + 2] cycloaddition products show calculated $\nu(N{=}C)$ modes at 1637 and 1418 cm^{-1}, respectively. Notably, the $\nu(N{\equiv}C)$ peak of surface-bound TBIC is blue-shifted from that of TBIC vapor at 2134 cm^{-1}.[37] This blue shift is explained by σ-donation of the lone pair molecular orbital of isocyanide—a state that possesses partial C−N antibonding character[38]—to the π^* state of Ge(100)-2 × 1 localized on the down atom.[39] These frontier orbitals are visualized in Figure 3. CO, isoelectronic to isocyanides, was reported to have similar configurations on the (100)-2 × 1 surfaces of Si and Ge.[40,41] Upon a higher exposure of 10 L, this $\nu(N{\equiv}C)$ peak exhibits a red shift to 2179 cm^{-1} (Figure 2). A similar coverage-dependent red shift was also found in our calculations where the peak at 2192 cm^{-1} for 0.5 ML moves to 2183 cm^{-1} at 1 ML, where one ML refers to one adsorbate per a dimer. This coverage-dependent red shift of $\nu(N{\equiv}C)$ is explained by the effect of electron density donated from adsorbed molecules weakening adjacent adsorbate−surface bonds.[42,43]

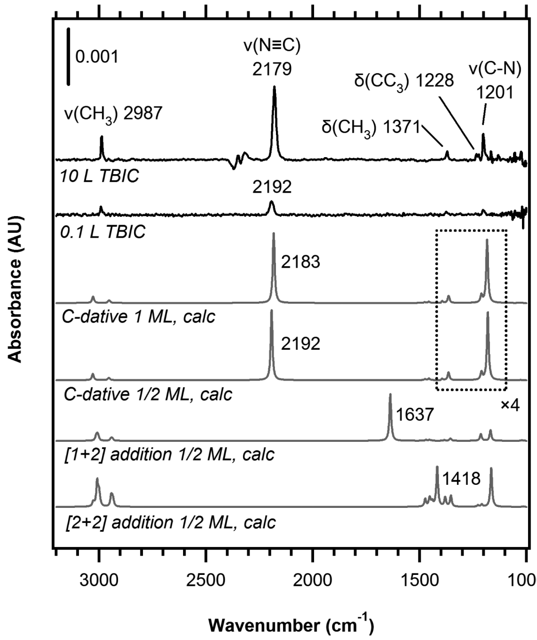


Figure 2. Experimental and DFT-calculated FTIR spectra of TBIC adsorbed on Ge(100)-2 × 1. The features around 2350 cm^{-1} are due to residual CO_2 (g) present in the purge boxes.

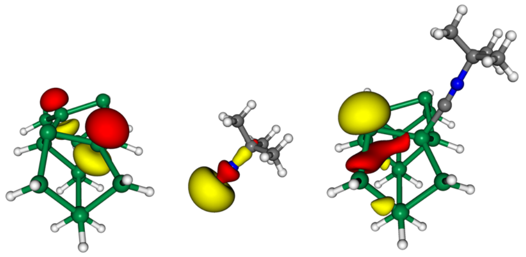

(a) $Ge_{15}H_{16}$ LUMO*
(b) TBIC HOMO
(c) TBIC + $Ge_{15}H_{16}$ HOMO

Figure 3. (a) LUMO (lowest unoccupied molecular orbital) of the $Ge_{15}H_{16}$ cluster, (b) HOMO (highest occupied molecular orbital) of a free TBIC molecule, and (c) HOMO of TBIC adsorbed on $Ge_{15}H_{16}$ cluster. Red and yellow, molecular orbital isosurfaces of different signs; green, Ge; blue, N; gray, C; and white, H.

The explanation of dative bond formation of TBIC by σ-donation to the dimer π^* orbital is corroborated by analysis of the DFT-calculated geometries of the C-dative structure (Table 1). Our calculations accurately reproduce the bond lengths of N≡C in the TBIC molecule[44] and of the Ge dimer[45] in their

Table 1. Experimental and Calculated Bond Lengths and Vibrational Frequencies of the Isocyanide Moiety of TBIC and of the Ge Dimer

		free		C-dative	
		N≡C	Ge dimer	N≡C	Ge dimer
bond length (Å)	expt	1.167[a]	2.5[b]	–	–
	calcd	1.170	2.474	1.159	2.592
vibrational frequency (cm^{-1})	expt	2134[c]	227[d]	2192	–
	calcd	2137	243	2192	206

[a] Reference 44. [b] Reference 45. [c] Reference 37. [d] Dimer stretch and backbond twist, ref 47.

"free" states without adsorption interaction. Upon C-dative bond formation of TBIC, the Ge dimer is elongated, whereas the isocyanide group contracts. These changes are also explained by donation of the isocyanide lone pair electrons to the Ge(100)-2 × 1 surface π^* state, such that the bond strength of C−N increases while that of Ge−Ge decreases. It is known that strengths and stretching frequencies of chemical bonds are inversely related to their lengths.[46] The validity of our calculations is supported by an accurate prediction of $\nu(\mathrm{N{\equiv}C})$ in both free and adsorbate configurations (Table 1).

Figure 4 shows TPD spectra of 1 L TBIC adsorbed on Ge(100)-2 × 1. We observe a single, broad peak corresponding to molecular desorption of TBIC (m/e = 83). Since the yield of this parent ion is small,[32] several fragments were also recorded during the TPD scan, among which the peak with the highest intensity (m/e = 41) is presented in Figure 4. All recorded ions had a single peak centered at 417 K. With a simple Redhead analysis[48] employing a typical preexponential factor of 10^{13} s^{-1}, this peak desorption temperature translates into a desorption energy (E_{des}) of 26.8 kcal/mol, which can be approximated as negative of the adsorption energy (E_{ads}) since formation and breaking of the dative bond is not an activated process (see below).

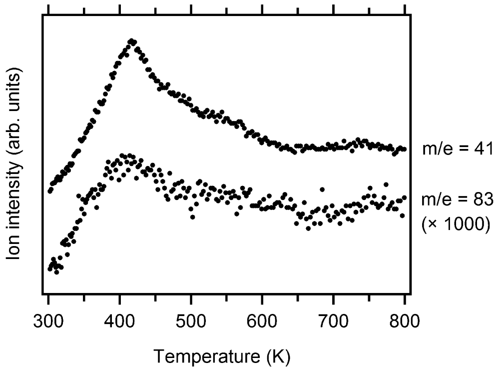


Figure 4. TPD spectra collected following 1 L TBIC adsorption on Ge(100)-2 × 1 at room temperature.

The calculated E_{ads} for three possible structures of TBIC on Ge(100)-2 × 1 are shown in Figure 5. Among those shown, only the C-dative bond structure is stable enough to be detectable in our experimental time scale of minutes. The DFT-calculated E_{ads} of −25.0 kcal/mol is close to the experimental E_{ads} (−26.8 kcal/mol). Also, we could not locate a transition state between the reactants (separated cluster and TBIC molecule) and the C-dative bond structure, suggesting the adsorption process is nonactivated.[49]

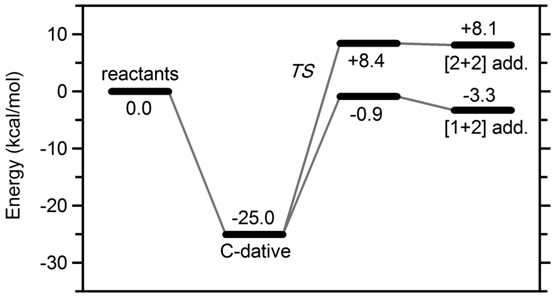


Figure 5. Calculated adsorption energies of TBIC on Ge(100)-2 × 1. TS: transition states.

Recently, dative bond energies of various organic molecules on group 14 semiconductor surfaces were tabulated in ref 3. To our knowledge, the E_{ads} = −26.8 kcal/mol of TBIC is the largest reported experimental formation energy of a single dative bond on Ge(100)-2 × 1 so far, and is even comparable to the strongest dative bond reported on Si, where E_{ads} of organic molecules are systematically larger than those on Ge.[3] This is in line with the periodic trends found with adsorption of other organic molecules on group 14 semiconductor surfaces.[3,4] In general, dative bonding through N yields a larger E_{ads} than through O of analogous adsorbates, because N has lower electronegativity, and thus a greater propensity for donation of electron density. Dative bonding of an organic molecule through C, which has never been experimentally observed on group 14 semiconductor surfaces because of the rarity of C lone pair electrons, potentially has an even larger E_{ads}, since C has lower electronegativity than N.

In conclusion, strong dative bond formation of TBIC on Ge(100)-2 × 1 was identified by FTIR spectroscopy, TPD, and DFT techniques. The vibrational features and geometries of TBIC adsorbates reveal the σ-donating nature of the C−Ge bonding. This dative bond through a C atom has a large adsorption energy—the strongest yet reported for a dative bond to the surface—as confirmed by both desorption experiments and calculations. The direct surface-carbon dative bond formed by isocyanide, analogous to the organometallic chemistry of low-coordinate germanium, broadens the current understanding of organic−semiconductor interaction and may be utilized in future semiconductor functionalization schemes.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the National Science Foundation (CHE-1213879). B.S. acknowledges the Samsung Scholarship for fellowship support. Scientific discussions with T. Sandoval were highly appreciated.

■ REFERENCES

(1) Loscutoff, P. W.; Bent, S. F. *Annu. Rev. Phys. Chem.* **2006**, *57*, 467.
(2) Yoshinobu, J. *Prog. Surf. Sci.* **2004**, *77*, 37.
(3) Kachian, J. S.; Wong, K. T.; Bent, S. F. *Acc. Chem. Res.* **2010**, *43*, 346.
(4) Min, Y. H.; Lee, H.; Kim, D. H.; Kim, S. In *Functionalization of Semiconductor Surfaces*; Tao, F., Bernasek, S. L., Eds.; Wiley: Hoboken, NJ, 2012; p 193.
(5) Nenajdenko, V. G. *Isocyanide Chemistry: Applications in Synthesis and Material Science*; Wiley: Weinheim, Germany, 2012.
(6) Angelici, R. J.; Lazar, M. *Inorg. Chem.* **2008**, *47*, 9155.
(7) Lazar, M.; Angelici, R. J. In *Modern Surface Organometallic Chemistry*; Basset, J.-M., Psaro, R., Roberto, D., Ugo, R., Eds.; Wiley: Weinheim, Germany, 2009; p 513.
(8) Kuznetsov, M. L. *Russ. Chem. Rev.* **2002**, *71*, 265.

(9) Singleton, E.; Oosthuizen, H. E. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, NY, 1983; Vol. *22*, p 209.

(10) Hong, S.; Reifenberger, R.; Tian, W.; Datta, S.; Henderson, J.; Kubiak, C. P. *Superlattices Microstruct.* **2000**, *28*, 289.

(11) Seminario, J. M.; De La Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616.

(12) Tan, A.; Balachandran, J.; Sadat, S.; Gavini, V.; Dunietz, B. D.; Jang, S.-Y.; Reddy, P. *J. Am. Chem. Soc.* **2011**, *133*, 8838.

(13) Hofmann, O. T.; Deinert, J.-C.; Xu, Y.; Rinke, P.; Stähler, J.; Wolf, M.; Scheffler, M. *J. Chem. Phys.* **2013**, *139*, 174701.

(14) Yang, S.; Prendergast, D.; Neaton, J. B. *Nano Lett.* **2012**, *12*, 383.

(15) Kugler, T.; Ziegler, C.; Göpel, W. *J. Mol. Struct.* **1993**, *293*, 257.

(16) Kugler, T.; Ziegler, C.; Göpel, W. *Mater. Sci. Eng., B* **1996**, *37*, 112.

(17) Yokelson, H. B.; Millevolte, A. J.; Haller, K. J.; West, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1605.

(18) Redondo, A.; Goddard, W. A., III. *J. Vac. Sci. Technol., A* **1982**, *21*, 344.

(19) Verwoerd, W. S.; Weimer, K. *J. Comput. Chem.* **1991**, *12*, 417.

(20) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168.

(21) Brown, Z. D.; Vasko, P.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2012**, *134*, 4045.

(22) Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85.

(23) Loscutoff, P. W.; Wong, K. T.; Bent, S. F. *J. Phys. Chem. C* **2010**, *114*, 14193.

(24) Loscutoff, P. W.; Wong, K. T.; Bent, S. F. *Surf. Sci.* **2010**, *604*, 1791.

(25) Choi, K.; Buriak, J. M. *Langmuir* **2000**, *16*, 7737.

(26) Cullen, G. W.; Amick, J. A.; Gerlich, D. *J. Electrochem. Soc.* **1962**, *109*, 124.

(27) Lefèvre, X.; Segut, O.; Jégou, P.; Palacina, S.; Jousselme, B. *Chem. Sci.* **2012**, *3*, 1662.

(28) Filler, M. A.; Keung, A. J.; Porter, D. W.; Bent, S. F. *J. Phys. Chem. B* **2006**, *110*, 4115.

(29) Teplyakov, A. V.; Lal, P.; Noah, Y. A.; Bent, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 7377.

(30) Mui, C.; Han, J. H.; Wang, G. T.; Musgrave, C. B.; Bent, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 4027.

(31) Filler, M. A.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. C* **2007**, *111*, 1739.

(32) Heerma, W.; de Ridder, J. J. *Org. Mass Spectrom.* **1970**, *3*, 1439.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Rev. D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(34) Andersson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937.

(35) Peng, C.; Schlegel, H. B. *Isr. J. Chem.* **1993**, *33*, 449.

(36) Varetto, U. *MOLEKEL 5.4.0.8*; Swiss National Supercomputing Centre: Lugano, Switzerland, 2009.

(37) Horrocks, W. D., Jr.; Mann, R. H. *Spectrochim. Acta* **1963**, *19*, 1375.

(38) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 1803.

(39) Gurlu, O.; Zandvliet, H. J. W.; Poelsema, B. *Phys. Rev. Lett.* **2004**, *93*, 066101.

(40) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, *21*, 137.

(41) He, J. H.; Zhang, Y. P.; Mao, W.; Xu, G. Q.; Tok, E. S. *Surf. Sci.* **2012**, *606*, 784.

(42) de Paola, R. A.; Hoffmann, F. M.; Heskett, D.; Plummer, E. W. *Phys. Rev. B* **1987**, *35*, 4236.

(43) Widjaja, Y.; Musgrave, C. B. *J. Chem. Phys.* **2004**, *120*, 1555.

(44) Howard, N. W.; Legon, A. C.; Rego, C. A.; Wallwork, A. L. *J. Mol. Struct.* **1989**, *197*, 181.

(45) Shirasawa, T.; Mizuno, S.; Tochihara, H. *Surf. Sci.* **2006**, *600*, 815.

(46) Cremer, D.; Kraka, E. *Curr. Org. Chem.* **2010**, *14*, 1524.

(47) Räthel, J.; Speiser, E.; Esser, N.; Bass, U.; Meyer, S.; Schäfer, J.; Geurts, J. *Phys. Rev. B* **2012**, *86*, 035312.

(48) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(49) Mui, C.; Musgrave, C. B. *Langmuir* **2005**, *21*, 5230.