Adsorption of Structural and Stereoisomers of Cyclohexanediamine at the Ge(100)-2×1 Surface: Geometric Effects in Adsorption on a Semiconductor Surface

Keith T. Wong and Stacey F. Bent[*]

Department of Chemical Engineering, Stanford University, 381 North-South Mall, Stanford, CA 94305

[*]Corresponding author. E-mail address: sbent@stanford.edu

A. Cyclohexanediamine Multilayer XP Spectra

XP spectra of physisorbed multilayers of each cyclohexanediamine isomer are shown in Figure S1. The C(1s) spectra are well fit by two peaks with the higher binding energy peak having one half the area of the lower binding energy peak, as with the chemisorbed C(1s) spectra in Figure S3. The N(1s) spectra of physisorbed multilayers were all fit by a single component since the two amines are chemically indistinguishable. The binding energy of this N(1s) peak was 399.0-399.2 eV, which provides a reference for the binding energy of unreacted amines.
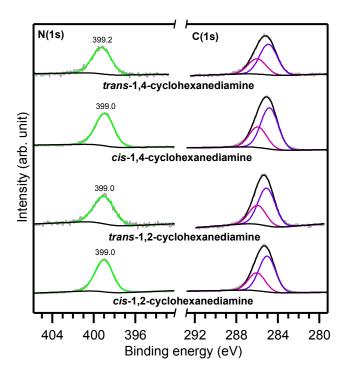

Figure S1. XP Spectra of N(1s) and C(1s) photoelectron regions of physisorbed multilayers of cyclohexanediamine isomers at low temperature on Ge(100). Spectra have been scaled to roughly the same peak height, and binding energies have been corrected for surface charging.

B. Cyclohexylamine XP Spectra

Cyclohexylamine N(1s) and C(1s) XP spectra are shown in Figure S2. The C(1s) spectrum is fit to two components with the ratio of the high binding energy to low binding energy peak areas fixed to 1:5 to represent carbon bonded to nitrogen and the remaining carbons in the cyclohexane ring. The C:N peak area is 6:1.0 as expected for cyclohexylamine. Since unreacted amines cannot be present at the surface for chemisorbed monofunctional amines, the N(1s) spectrum should be fit by two peaks, and this is what is found using the same fitting procedure as for cyclohexanediamines. The peaks are located at 397.8 and 400.2 eV and provide a reference for the binding energies for N–H dissociated and N dative bonded amines, respectively.
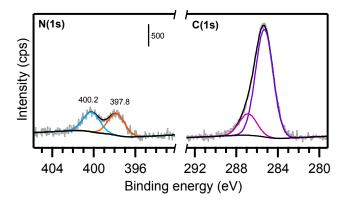

Figure S2. XP spectra of N(1s) and C(1s) photoelectron region for Ge(100)-2×1 exposed to 100 L (greater than a saturation dose) of cyclohexylamine at room temperature.

C. Cyclohexanediamine C(1s) XP Spectra

XP spectra for the C(1s) photoelectron region after exposure to the four cyclohexanediamine isomers were also collected and are shown in Figure S3. These spectra were well fit by two peaks. The lower binding energy peak is located at 284.8-285.1 eV and is attributed to the four carbon atoms in the cyclohexane ring bonded only to other carbon atoms and hydrogen. The higher binding energy peak (285.9-286.1 eV) was fixed to have one half the peak area of the lower binding energy peak and corresponds to the two carbon atoms in the cyclohexane ring bonded to amine nitrogens. The C(1s) peak is expected to lie at higher binding energy for these carbon atoms due to reduced electron density from the higher electronegativity of nitrogen (compared to hydrogen).

The total integrated area of the C(1s) peaks can be compared to the total area of N(1s) peaks from Figure 2 to calculate the elemental ratio. The ratio of carbon to nitrogen (carbon normalized to 6) was found to be 6:1.9, 6:2.2, 6:2.3, and 6:2.3 for *trans*-1,4-, *cis*-1,4-, *trans*-1,2-, and *cis*-1,2-cyclohexanediamine, respectively. These are all close to the expected ratio of 6:2 for cyclohexanediamines.
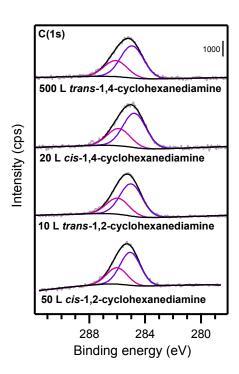

Figure S3. C(1s) XP spectra of Ge(100)-2×1 exposed to a saturation dose of cyclohexanediamine isomers at room temperature. Data are from the same experiments as the N(1s) XP spectra shown in Figure 1.

D. Calculated NH$_2$ Scissor Mode Frequencies

DFT calculations for cyclohexanediamines show that the NH$_2$ scissor mode red-shifts from its frequency for a free amine upon forming a dative bond to the Ge(100)-2×1 surface (see Figure 3). However, using cyclohexylamine as a simpler test molecule, we have found that the degree of red-shifting is strongly dependent on the adsorbate's orientation. Table S1 shows the calculated frequency of the NH$_2$ scissor mode for a free cyclohexylamine molecule and for cyclohexylamine dative bonded to a Ge$_{23}$H$_{24}$ cluster in two different orientations. The two geometries are called "standing up" and "lying down", as in one case the cyclohexane ring stands up away from the surface, and in the other case the cyclohexane ring is tilted towards the surface. The two orientations are shown in Figure S4. The adsorption energies of these two orientations differ negligibly (0.1 kcal/mol), as shown in Table S1, but the red-shift of the NH$_2$ scissor peak ranges from 13 to 23 cm^{-1}. The degree of red-shifting may also be affected by other factors such as coupling of NH$_2$ scissoring between amines adsorbed on neighboring surface sites or, as mentioned in the main text, weakening of the N–Ge dative bond due to nonlocal interactions between adsorbates on neighboring dimers. The end result is that the NH$_2$ scissor mode does not provide reliable information regarding the state of amines at the surface.

Table S1. DFT calculated NH$_2$ scissor frequency of a free cyclohexylamine molecule and of cyclohexylamine dative bonded on a Ge$_{23}$H$_{24}$ cluster in two different orientations. The red-shift of the NH$_2$ scissor mode from the free molecule to the two dative bonded products and the calculated adsorption energy of each product are also shown.

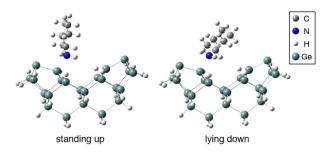|	δ_{sc}(NH$_2$) frequency (cm^{-1})	δ_{sc}(NH$_2$) red-shift from free molecule (cm^{-1})	Adsorption energy (kcal/mol)
Free cyclohexylamine	1591	-	-
N dative/Ge$_{23}$H$_{24}$ (standing up)	1568	23	23.4
N dative/Ge$_{23}$H$_{24}$ (lying down)	1578	13	23.3

Figure S4. DFT optimized geometries of cyclohexylamine dative bonded to a Ge$_{23}$H$_{24}$ cluster in two different orientations.

E. DFT Calculated Monodentate Adsorption Energies

Table S2. An expanded version of Table 1 showing DFT calculated adsorption energies for cyclohexylamine and six cyclohexanediamine isomers adsorbed on a $Ge_{23}H_{24}$ cluster. For the diamines, only one functional group is reacted with the cluster.

	Calculated adsorption energy (kcal/mol)	
	N dative bonded	N–H dissociated
cyclohexylamine	-23.4	-30.6
cis-1,2-cyclohexanediamine	-28.1	-29.6
trans-1,2-cyclohexanediamine	-27.6	-31.2
cis-1,3-cyclohexanediamine	-23.2	-28.3
trans-1,3-cyclohexanediamine	-23.5	-30.4
cis-1,4-cyclohexanediamine	-21.3	-28.4
trans-1,4-cyclohexanediamine	-23.0	-31.4

F. Uncorrected DFT Calculated Adsorption Energies

Table S3. DFT calculated adsorption energies without zero-point energy correction.

	Calculated adsorption energy (kcal/mol)					
	N dative	N dative/ N dative	1st N–H diss. TS	N–H diss./ N dative	2nd N–H diss. TS	N–H diss./ N–H diss.
cyclohexylamine	-25.6	-	3.7	-	-	-
cis-1,2-cyclohexanediamine	-30.0	-37.2	-9.6	-53.7	-12.3	-53.5
trans-1,2-cyclohexanediamine	-29.6	-36.4	-8.0	-52.5	-13.6	-53.8
cis-1,4-cyclohexanediamine	-23.3	-31.5	-4.6	-39.1	-12.2	-43.5
trans-1,4-cyclohexanediamine	-25.0	-25.3	-2.8	-36.1	-3.1	-38.1

Complete Reference 46:

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; 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 ed.; Gaussian, Inc.: Wallingford, CT, 2004.