University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track

Written Qualifying Exam
June 18, 2007

Physical Chemistry I

Questions are based on the following article:

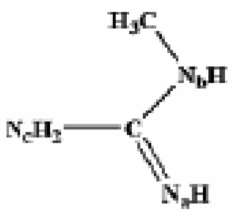
> "Attachment of Alanine and Arginine to the Ge(100)-2×1 Surface" Pendar Ardalan, Nazanin Davani, and Charles B. Musgrave. *Journal of Physical Chemistry C*, **2007**, 111(9), 3692-3699.

1. The paper discusses the nature of the clean group IV (100) 2×1 reconstructed surfaces. What does this mean? Be sure to discuss the (100) surface before and after reconstruction paying special attention to where the atoms are and how they are connected. Also discuss the mechanism and driving force for this reconstruction process. Why are semiconducting surfaces more likely to reconstruct than metal surfaces.

2. Devise an experiment that will prove or disprove the hypothesis put forth in this paper. If the hypothesis of this paper is correct, what results do you expect from your proposed experiments?

3. Table three describes vibrational frequencies computed for the arginine's imine N dative bonded states at the Ge(100)-2×1 surface. They are summarized in the following table:

Product	N_aH_a stretch	N_bH_b stretch	N_cH_{c2} stretch
Imine N dative bond, Cis-conformer	3466 cm^{-1}	3169 cm^{-1}	3591cm^{-1}, 3490 cm^{-1}
Imine N dative bond, Trans-conformer	3458 cm^{-1}	3513 cm^{-1}	3564 cm^{-1}, 3452 cm^{-1}



Please explain why these vibrational frequencies are all so very different from the reported NH stretch of gas phase ammonia at 3335 cm^{-1}? Also explain why these vibrational frequencies are all so very different from each other.

4. This article discusses the differences between kinetic control and thermodynamic control of the reaction pathways. What are the main driving forces that distinguish these different pathways? Please describe completely one system that exemplifies the differences between kinetic control and thermodynamic control of reaction pathways. (Do not use an example from this paper.)

5. Define and discuss dative bonding, especially with regard to this article. The authors claim

> “Both glycine and alanine have the same reactivity because the C-C and C-H σ-bonds of their side chains do not react with Si or Ge (100)-2×1 surfaces except at high temperatures, and replacement of the H atom side chain with a methyl side chain has essentially no effect on the common group reactivity. On the other hand, the common group does react with these surfaces and in this study we explored several different possible reactions between alanine and the Ge(100)-2×1 surface. These include C+O and O-H dative bonding to the electrophilic down Ge atom of the dimer followed by O-H dissociation from each adsorbed state, direct [2+2] cycloaddition and [2+2] cycloadition proceeding through the C=O dative bonded state (Figure 2).”

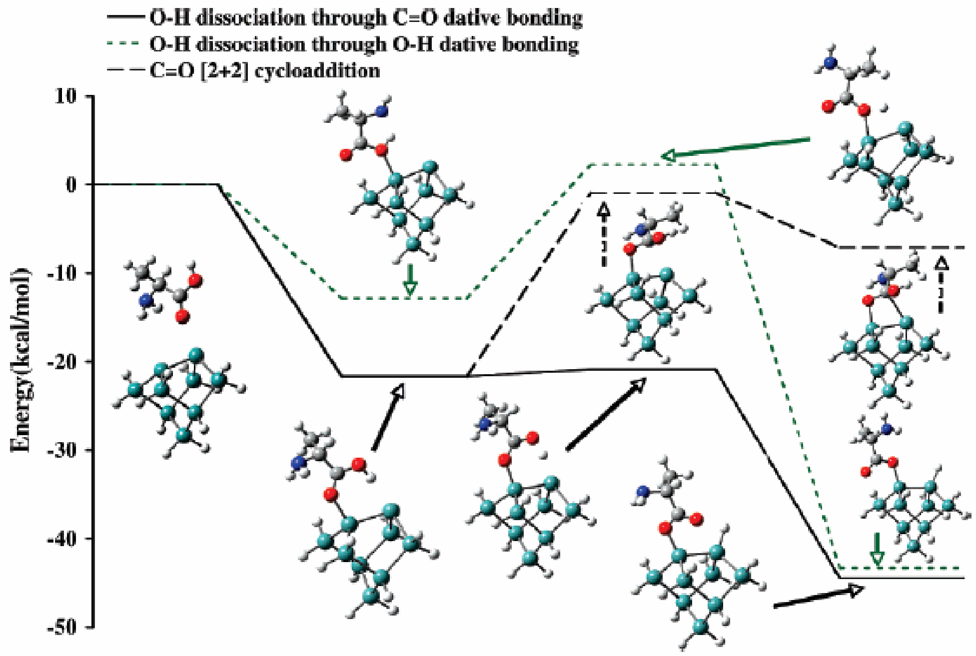


Figure 2. O−H dissociation and C=O [2+2] cycloaddition reactions of alanine on the Ge(100)-2×1 surface.

Sketch (with arrows describing electron movement) very clearly the bond formations and breakages described by O-H dissociation through O-H dative bonding of alanine on the Ge(100)-2×1 surface as described by figure 2. (Hint: Use figure 10 as a guide for how to sketch the diagram.)

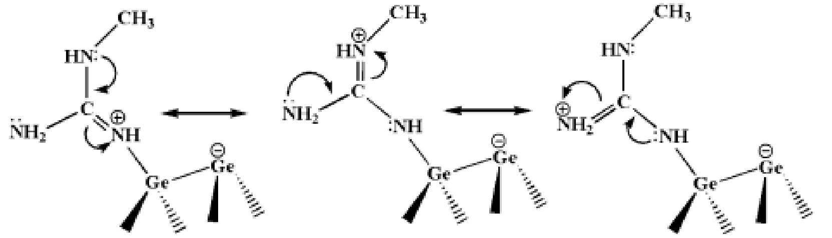


Figure 10. Resonance model representing the dative bonding of *N*-methylguanidine to the Ge(100)-2×1 surface via its imine nitrogen atom.

6. Table 1 describes the calculated vibrational frequencies of the OH dissociated and amine and carbonyl adsorption products of alanine at the Ge(100)-2×1 surface. Please sketch the absorption infrared spectrum of the species hypothesized by the authors to be the majority product on the surface when alanine reacts with the Ge(100)-2×1 surface.

7. (Green Chemistry Question) How can theoretical studies contribute to the advancement of green chemistry? Please give at least one detailed example.

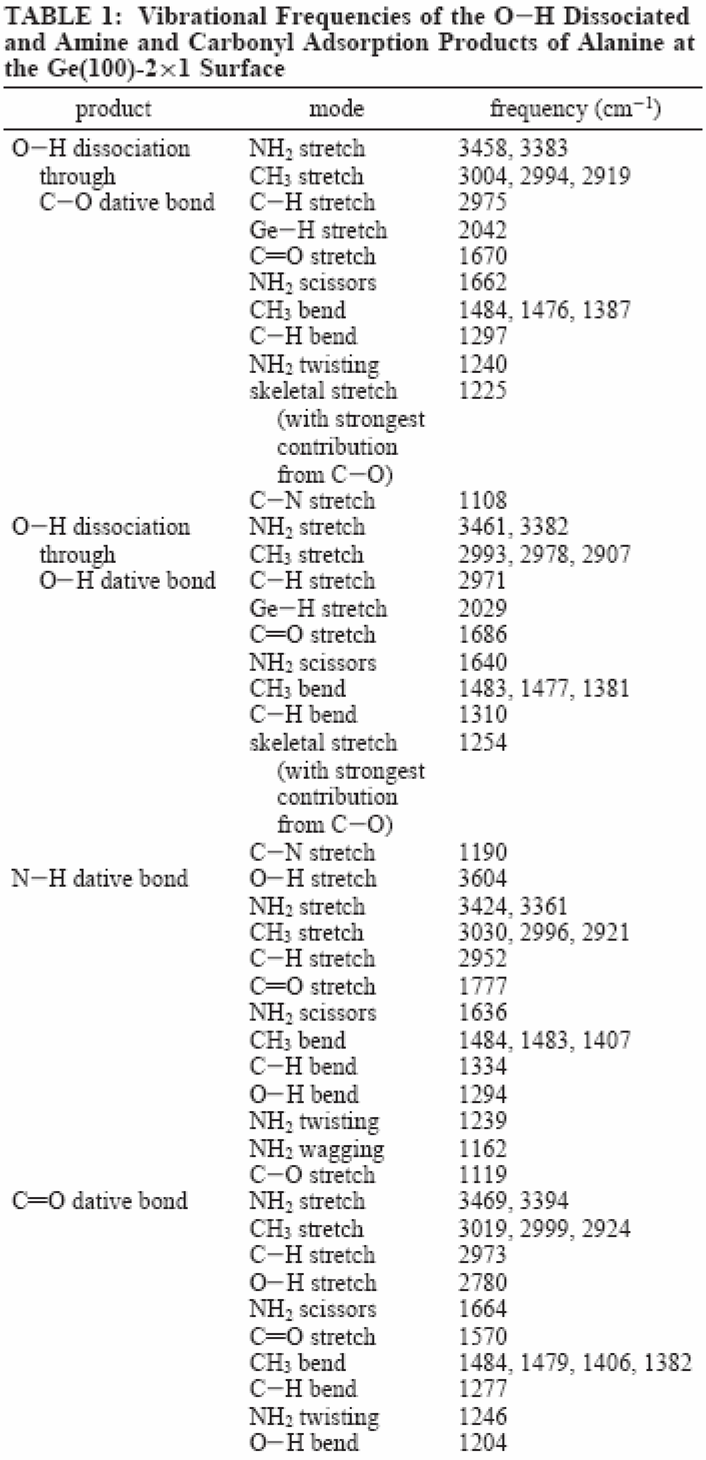


TABLE 1: Vibrational Frequencies of the O−H Dissociated and Amine and Carbonyl Adsorption Products of Alanine at the Ge(100)-2×1 Surface

product	mode	frequency (cm^{-1})
O−H dissociation through C−O dative bond	NH_2 stretch	3458, 3383
	CH_3 stretch	3004, 2994, 2919
	C−H stretch	2975
	Ge−H stretch	2042
	C=O stretch	1670
	NH_2 scissors	1662
	CH_3 bend	1484, 1476, 1387
	C−H bend	1297
	NH_2 twisting	1240
	skeletal stretch (with strongest contribution from C−O)	1225
	C−N stretch	1108
O−H dissociation through O−H dative bond	NH_2 stretch	3461, 3382
	CH_3 stretch	2993, 2978, 2907
	C−H stretch	2971
	Ge−H stretch	2029
	C=O stretch	1686
	NH_2 scissors	1640
	CH_3 bend	1483, 1477, 1381
	C−H bend	1310
	skeletal stretch (with strongest contribution from C−O)	1254
	C−N stretch	1190
N−H dative bond	O−H stretch	3604
	NH_2 stretch	3424, 3361
	CH_3 stretch	3030, 2996, 2921
	C−H stretch	2952
	C=O stretch	1777
	NH_2 scissors	1636
	CH_3 bend	1484, 1483, 1407
	C−H bend	1334
	O−H bend	1294
	NH_2 twisting	1239
	NH_2 wagging	1162
	C−O stretch	1119
C=O dative bond	NH_2 stretch	3469, 3394
	CH_3 stretch	3019, 2999, 2924
	C−H stretch	2973
	O−H stretch	2780
	NH_2 scissors	1664
	C=O stretch	1570
	CH_3 bend	1484, 1479, 1406, 1382
	C−H bend	1277
	NH_2 twisting	1246
	O−H bend	1204