

Molecular dissociation of group-V hydrides on Si(001)

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We present a comparative *ab initio* survey of possible dissociation products of NH₃, PH₃, and AsH₃ on the Si(001) surface. In agreement with previous studies, we find that the relative energetics of XH₃ and XH₂ species (X=N, P, As) are common across all three systems. In contrast, the energetics of the onward dissociation into XH and X species differs markedly between nitrogen on the one hand, and phosphorus and arsenic on the other.

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The Group V elements nitrogen, phosphorus, and arsenic are important additives in the fabrication of silicon semiconductor devices. Doping with phosphorus and arsine provides *n*-type charge carriers, whereas the introduction of nitrogen leads to ultrathin Si₃N₄, which has numerous semiconductor applications such as gate dielectrics, insulators, and oxidation masks.¹⁻³ These elements are commonly introduced to the silicon surface in the form of their hydrides (ammonia, phosphine, and arsine) in chemical vapor deposition or molecular beam epitaxy schemes. Recently, significant progress has been made in the theoretical understanding of the dissociation chemistry of ammonia and phosphine on the Si(001) surface. This knowledge is of particular relevance to the fabrication of atomic-scale devices such as atomic wires, single electron transistors, and quantum computers.^{4,5}

Ammonia on Si(001) has been well-studied, and it is now firmly established both theoretically⁶⁻¹² and experimentally¹³⁻¹⁷ that ammonia chemisorbs as NH₃ and rapidly dissociates into NH₂ and H at room temperature. However, the onward decomposition involving NH and N species is the subject of controversy, and an unambiguous dissociation pathway has yet to be established. Xu *et al.*^{10,11} performed single-dimer cluster calculations and found the preferred structure consisted of a nitrogen interstitial linking the first and second layers. However, similar cluster calculations by Widjaja and Musgrave¹⁸ found this structure was endothermic with respect to surface-bound NH₂+H, a result which is supported by slab calculations from Kim *et al.*¹²

Phosphine on Si(001) has also been extensively studied, and like ammonia, is known from experiments^{19,20} and theoretical calculations^{21,22} to chemisorb as PH₃ and rapidly dissociate into PH₂ and H at room temperature. It was initially thought that significantly elevated temperatures were required for further dissociation, but recent comprehensive scanning tunneling microscopy (STM) experiments^{23,24} at room temperature identified a number of distinct dissociation species as prominent features. Using density-functional calculations, these features were characterized as PH₂+H, PH+2H and P+3H species on the basis of a comprehensive survey of possible dissociation products.^{23,25} Notably, the experimental STM features matched the low-energy structures identified as thermodynamically favorable.

In comparison, arsine on Si(001) has received relatively minor attention. The only experimental study is by Kipp *et al.*²⁶ who performed photoemission and STM studies in conjunction with a short theoretical study by Northrup.²⁷ Miotto *et al.*²¹ also performed a comparative *ab initio* study which found that, in similarity with NH₃ and PH₃, arsine chemisorbs as AsH₃ and rapidly dissociates into AsH₂ and H.

In this work we present a systematic theoretical study which considers potential dissociation products of XH₃ (X=N, P, As) in an effort to tie together existing knowledge of these isoelectronic Group V hydrides on Si(001). Using density functional methods as applied in our previous studies of phosphine,^{23,25} a survey of structures is undertaken to calculate the energies of local minima on the potential energy surface, in the expectation that prominent intermediates in the dissociation pathway are to be found among the low-energy structures. Significantly, we find that the energetics of the most probable dissociation pathway differ substantially for nitrogen as compared to phosphine and arsine.

The calculations in this work were performed with the VASP package,²⁸⁻³⁰ using ultra-soft pseudopotentials³¹ and the generalized gradient approximation (PW91 functional³²). The Si surface was represented using a six-layer slab model in a 2×4 supercell, containing four surface Si-Si dimers in one dimer row, and a vacuum region equivalent to six atomic layers. Our previous phosphine studies^{23,25} show that the 2×4 cell used in this work is well converged with respect to the energy differences between the principal structures of interest. The calculations employed a 250 eV cutoff for the plane-wave basis set and the **k**-space integration was performed on a 2×1×1 Monkhorst-Pack grid.³³ The back surface was passivated with a dihydride structure, and all atoms except the bottom silicon layer and the passivating hydrogens were allowed to relax.

We consider XH_x bonding at four sites on the Si(001) surface, which gives rise to five principal bonding configurations shown in Fig. 1. Permutations arising from the placement of the XH_x group and the 3-x hydrogens lead to a large number of structural isomers, and the full set of structures considered in the survey are indicated in Fig. 2. This set of structures specifically excludes unstable configurations, and

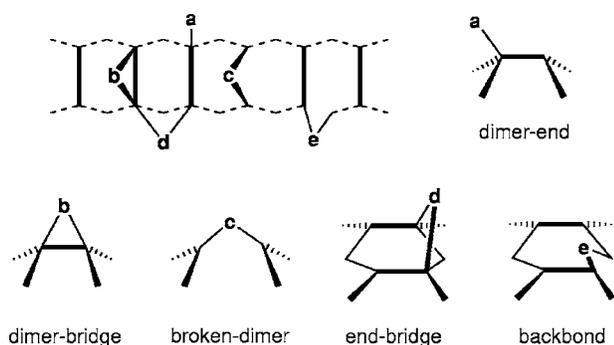


FIG. 1. Schematic top and perspective views of principal bonding sites of XH_x units ($X=N, P, As$; $x=0, 1, 2, 3$) on the Si(001) surface. (a) binds in the *dimer-end* position at one end of a Si-Si surface dimer. (b) binds to two Si atoms of the same dimer forming a triangular *dimer-bridge* structure. Similar to a dimer-bridge, (c) in a *broken-bridge* configuration is bound to two Si atoms on the same dimer, however the Si-Si dimer bond is broken; in effect (c) inserts itself into the dimer bridge. In an *end-bridge* configuration, (d) binds to two Si atoms of two adjacent dimers thereby bridging between two dimers. Finally, in a *backbond* configuration, (e) inserts between first and second layer Si atoms.

where multiple buckling options exist for the bare Si dimers, the most stable orientation is used. The structures are classified into groups which reflects the number of hydrogen atoms covalently bound to the X species. Structures in Groups A, B, C, and D thus contain XH_3 , XH_2 , XH , and X species, respectively.

The energies of the structures seen in Fig. 2 are listed in Table I and shown graphically in Fig. 3. For all three molecules the progressive dissociation leads to increasing energetic stability, indicating that complete dissociation of XH_3 into atomic species is thermodynamically favored. As might be expected on isoelectronic grounds, the initial stages of adsorption and dissociation (Groups A and B) are common across all three systems. However, Groups C and D do not continue this trend, and thus we can expect the onward dissociation mechanisms to progress along entirely different paths.

The only stable member of Group A is the A1 structure in which the XH_3 unit forms a dative bond with the Si down atom at a dimer-end site. Adsorption energies were computed using two separate calculations of the bare silicon surface and the gas-phase molecule, and the computed energies are typical as compared to a variety of previous slab^{6,21,23,25,27,34} and cluster^{6,8-10,20,23,25,35} calculations. Our adsorption energies for ammonia, phosphine, and arsine are 1.48, 0.90, and 0.71 eV, respectively, which compare well to literature values in the range 0.94–1.43 eV for ammonia,^{6,8-10,21,35} 0.56–1.08 eV for phosphine,^{20,21,23,25,34} and 0.56–1.0 eV for arsine.^{21,27}

Similar agreement across the three systems is seen for Group B, which consists of an XH_2 unit and a single hydrogen. There are a variety of stable configurations in Group B, but the most favored structure is B1, which is significantly more stable than A1, and is formed by a proton shift across the Si-Si dimer bond.^{8-10,21,35,36} Again, the results from this work compare well with previous calculations of the A1-B1

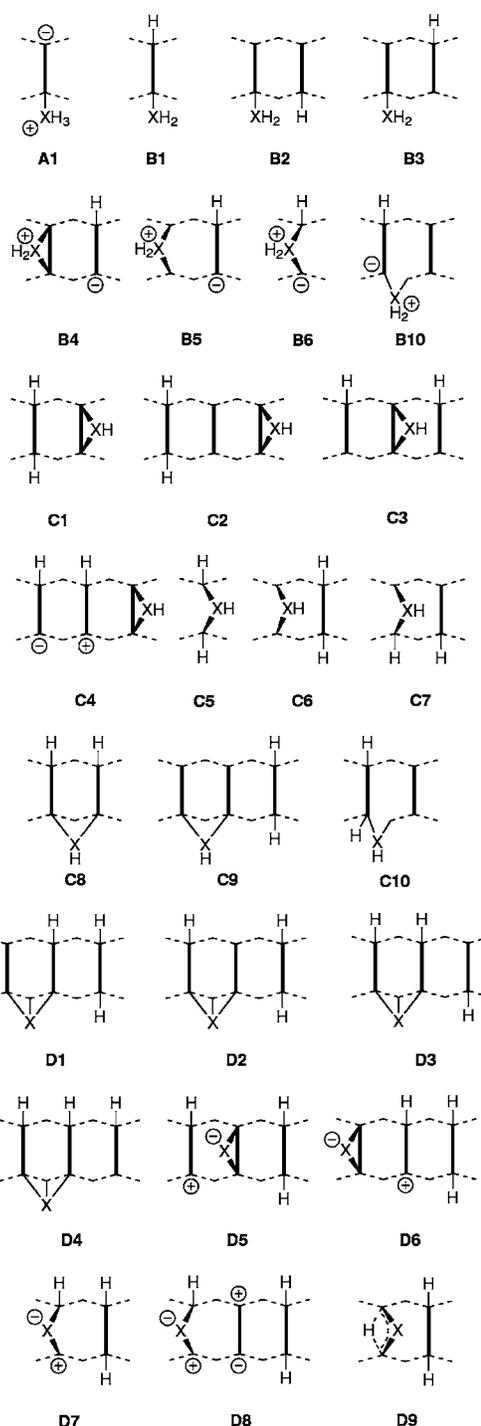


FIG. 2. Schematic structure diagrams of the XH_3 dissociation products considered in this work.

dissociation energy. Our dissociation energies for NH_3 (a), PH_3 (a), and AsH_3 (a) are 0.77, 1.14, and 1.44 eV, respectively, as compared to literature values 0.78–1.82 eV for ammonia,^{6,8-10,21,35} 1.10–1.69 eV for phosphine,^{21,23,25} and 1.91 eV for arsine.²¹

The most stable Group C structure for ammonia is the single-dimer wide C5 resulting from the insertion of a divalent NH group into the two Si atoms of a monohydride. Previous cluster calculations^{10,11,18} have also found C5 to be

TABLE I. Energies (in electron volts) of the dissociation structures considered in this work, expressed relative to A1 (surface adsorbed XH_3). Blank entries denote unstable structures.

Structure		N	P	As	Site
$XH_3(g)$		1.48	0.90	0.71	gas-phase
XH_3	A1	0.00	0.00	0.00	dimer-end
XH_2+H	B1	-0.77	-1.14	-1.44	dimer-end
	B2	-0.46	-0.81	-1.12	dimer-end
	B3	-0.40	-0.77	-1.08	dimer-end
	B4	-0.14	-0.59	-0.63	dimer-bridge
	B5		-0.38	-0.52	broken-dimer
	B6	-0.04	-0.56	-0.55	broken-dimer
	B10	0.38	0.01	0.02	backbond
$XH+2H$	C1	-1.04	-2.04	-2.55	dimer-bridge
	C2	-0.99	-2.00	-2.51	dimer-bridge
	C3	-0.63	-1.63	-2.14	dimer-bridge
	C4	-0.66	-1.67	-2.18	dimer-bridge
	C5	-1.19	-1.28	-1.65	broken-dimer
	C6	-0.49			broken-dimer
	C7	-0.88	-1.10	-1.50	broken-dimer
	C8	-0.39	-1.69	-2.28	end-bridge
	C9	0.01	-1.23	-1.83	end-bridge
	C10	-0.96	-0.97	-1.36	backbond
$X+3H$	D1	-0.93	-2.33	-2.97	end-bridge
	D2	-0.90	-2.32	-2.95	end-bridge
	D3	-0.51	-2.00	-2.65	end-bridge
	D4	-0.49	-2.00	-2.65	end-bridge
	D5	-1.11	-1.84	-2.55	dimer-bridge
	D6	-1.09	-1.80	-2.47	dimer-bridge
	D7	-1.23	-1.57	-2.16	broken-dimer
	D8	-1.28	-1.41	-1.96	broken-dimer
	D9	0.08	-1.23	-1.88	broken-dimer

the most stable NH structure. In contrast, C5 is one of the *least* stable structures for phosphine and arsine, and these systems instead prefer the C1 structure which is two dimers in width, and consists of XH in a dimer-bridge site with an adjacent monohydride. The stability of C1 for phosphine is

confirmed by bright centered features seen in numerous STM studies^{34,37–39} which have recently been unambiguously assigned as C1.^{23,25}

In Group D the X species is fully dehydrogenated, and the contrast between ammonia and the phosphine/arsine systems is even more prominent than for Group C. The most stable structure for ammonia (D8) is one of the least stable structures for phosphine and arsine, while conversely, the most stable structure for phosphine/arsine (D1) is disfavored for ammonia. Cluster calculations also find a D8-type structure (with N in a broken-dimer) as the stable end product when the nitrogen monomer remains surface adsorbed.^{10,11,18} Note however, that our study does not extend to the controversy over subsurface N interstitials, be they shallow or deep.¹² For phosphine and arsine, the most stable Group D structures are D1 and D2, in which the monomer is threefold coordinated at an end-bridge site. Experiments and theoretical calculations^{23,25} have conclusively identified D2 as a commonly observed feature in STM images, and it is not unreasonable to speculate that the arsine end-bridge feature observed in empty-state STM images by Kipp *et al.*²⁶ might be the D2 structure, and not C8 as suggested by Northrup.²⁷

We thus see that while the initial steps in the dissociation pathway are extremely similar for XH_3 and XH_2 adsorbates, the XH and X species exhibit quite different behavior for ammonia, as compared to phosphine and arsine. Insight into this situation comes from the stable structures, which for Groups A and B contain just a single Si–X bond, while in Groups C and D the most favorable configuration involves two or three Si–X bonds. This suggests that the covalent radius plays an important role for stabilization of competing structures. To quantify these size effects, we computed the Si–X distance in the molecule SiH_3-XH_2 and found bond lengths of 1.70, 2.36, and 2.38 Å for nitrogen, phosphorus, and arsenic, respectively. We thus see a natural pairing into phosphorus/arsenic on one hand, and nitrogen on the other—this is the same pairing as present in Groups C and D. As an illustration of this size effect, we consider the Si–X–Si triangular ring in the C1 structure, as preferred by phosphine and arsine. For ammonia, the much shorter N–Si bond length produces highly acute bond angles, leading to substantial ring strain which destabilizes C1 relative to C5. A similar argument explains the destabilization of the D1 structure for ammonia. Size effects are also significant for the backbond structure C10, which is reported to be an important low-energy intermediate in the dissociation of ammonia.^{10,18} In

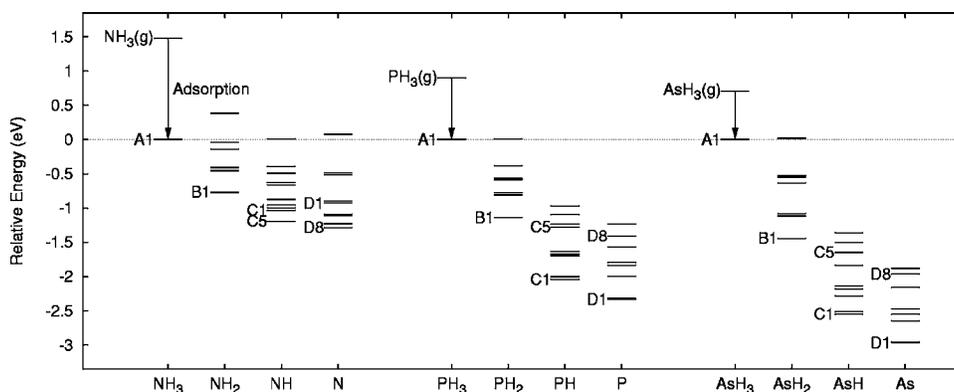


FIG. 3. Overview of computed energies for structures considered in this survey of NH_3 (left), PH_3 (center), and AsH_3 (right). Structures are ordered along the horizontal axis according to their degree of dissociation and vertically relative to the energy of the A1 structure for each species.

contrast, C10 is the least stable member in Group C for phosphine and arsine, and therefore of little relevance to the dissociation mechanism.

In summary, we have shown that the thermodynamically preferred configurations in the dissociation of phosphine and arsine are very similar, while the stable structures for ammonia differ substantially at the latter stages of dissociation. Although the exact details of the dissociation mechanism require knowledge of the transition-state barriers, we can reasonably expect that the phosphine and arsine dissociation mechanism will be similar. In contrast, the dissociation pathway for ammonia will progress along a markedly differ-

ent route. On a more general note, this work illustrates the utility of a systematic structure/energy surveys involving adjacent elements in the periodic table. As Fig. 3 shows, this approach provides a conceptual framework in which to understand surface chemistry and interpret both similarities and trends.

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- ¹E. Kooi, J. F. Vanlierop, and J. S. Appels, *J. Electrochem. Soc.* **123**, 1117 (1976).
- ²Y. Ma, T. Yasuda, and G. Lucovsky, *J. Vac. Sci. Technol. B* **11**, 1533 (1993).
- ³*Silicon Nitride in Electronics*, edited by V. I. Belyi, Vol. 34, Materials Science Monographs (Elsevier, New York, 1988).
- ⁴J. R. Tucker and T. C. Shen, *Int. J. Circuit Theory Appl.* **28**, 553 (2000).
- ⁵B. E. Kane, *Nature (London)* **393**, 133 (1998).
- ⁶S. H. Lee and M. H. Kang, *Phys. Rev. B* **58**, 4903 (1998).
- ⁷R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Phys. Rev. B* **58**, 7944 (1998).
- ⁸Y. Widjaja, M. M. Mysinger, and C. B. Musgrave, *J. Phys. Chem. B* **104**, 2527 (2000).
- ⁹Y. Widjaja and C. B. Musgrave, *Surf. Sci.* **469**, 9 (2000).
- ¹⁰X. Xu, S. Y. Kang, and T. Yamabe, *Phys. Rev. Lett.* **88**, 076106 (2002).
- ¹¹X. Xu, S. Y. Kang, and T. Yamabe, *Chem.-Eur. J.* **8**, 5351 (2002).
- ¹²H. -J. Kim and J. -H. Cho, *Phys. Rev. B* **69**, 233402 (2004).
- ¹³M. Fujisawa, Y. Taguchi, Y. Kuwahara, M. Onchi, and M. Nishijima, *Phys. Rev. B* **39**, 12918 (1989).
- ¹⁴J. L. Bischoff, F. Lutz, D. Bolmont, and L. Kubler, *Surf. Sci. Lett.* **248**, L240 (1991).
- ¹⁵M. J. Dresser, P. A. Tayler, R. M. Wallace, and W. J. Choyke, *Surf. Sci.* **218**, 75 (1989).
- ¹⁶N. Franco, J. Avila, M. E. Davila, M. C. Asensio, D. P. Woodruff, O. Schaff, V. Fernandez, K. M. Schindler, V. Fritzsche, and A. M. Bradshaw, *Phys. Rev. Lett.* **79**, 673 (1997).
- ¹⁷K. T. Queeney, Y. J. Chabal, and K. Raghavachari, *Phys. Rev. Lett.* **86**, 1046 (2001).
- ¹⁸Y. Widjaja and C. B. Musgrave, *Phys. Rev. B* **64**, 205303 (2001).
- ¹⁹M. L. Colaianni, P. J. Chen, and J. T. Yates, Jr., *J. Vac. Sci. Technol. A* **12**, 2995 (1994).
- ²⁰J. Shan, Y. Wang, and R. J. Hamers, *J. Phys. Chem.* **100**, 4961 (1996).
- ²¹R. Miotto, G. P. Srivastava, R. H. Miwa, and A. C. Ferraz, *J. Chem. Phys.* **114**, 9549 (2001).
- ²²R. Miotto, G. P. Srivastava, and A. C. Ferraz, *Phys. Rev. B* **63**, 125321 (2001).
- ²³H. F. Wilson, O. Warschkow, N. A. Marks, S. R. Schofield, N. J. Curson, P. V. Smith, M. W. Radny, D. R. McKenzie, and M. Y. Simmons, *Phys. Rev. Lett.* **93**, 226102 (2004).
- ²⁴N. J. Curson, S. R. Schofield, O. Warschkow, N. A. Marks, H. F. Wilson, P. V. Smith, M. W. Radny, D. R. McKenzie, and M. Y. Simmons (unpublished).
- ²⁵O. Warschkow, H. F. Wilson, N. A. Marks, S. R. Schofield, N. J. Curson, P. V. Smith, M. W. Radny, D. R. McKenzie, and M. Y. Simmons, *Phys. Rev. B* **72**, 125328 (2005).
- ²⁶L. Kipp, R. D. Bringans, D. K. Biegelsen, L.-E. Swartz, and R. F. Hicks, *Phys. Rev. B* **50**, 5448 (1994).
- ²⁷J. E. Northrup, *Phys. Rev. B* **51**, 2218 (1995).
- ²⁸G. Kresse and J. Hafner, *Phys. Rev. B* **47**, R558 (1993).
- ²⁹G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ³⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ³¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ³²J. P. Perdew, in *Electronic Structure of Solids 91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
- ³³H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ³⁴L. Kipp, R. D. Bringans, D. K. Biegelsen, J. E. Northrup, A. Garcia, and L. -E. Swartz, *Phys. Rev. B* **52**, 5843 (1995).
- ³⁵E. Fattal, M. Radeke, G. Reynolds, and E. Carter, *J. Phys. Chem. B* **101**, 8658 (1997).
- ³⁶Z. K. Smedarchina and M. Z. Zgierski, *Int. J. Mol. Sci.* **4**, 445 (2003).
- ³⁷Y. Wang, M. J. Bronikowski, and R. J. Hamers, *J. Phys.: Condens. Matter* **98**, 5966 (1994).
- ³⁸D.-S. Lin, T.-S. Ku, and T.-J. Sheu, *Surf. Sci.* **424**, 7 (1999).
- ³⁹N. J. Curson, S. R. Schofield, M. Y. Simmons, L. Oberbeck, J. L. O'Brien, and R. G. Clark, *Phys. Rev. B* **69**, 195303 (2004).