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► **To cite this version:**

Elie Geagea, Ali Hamadeh, Judicaël Jeannoutot, Frank Palmينو, Nicolas Breault, et al.. Dissociation of N₂ on a Si(111)-7x7 Surface at Room Temperature. *ChemPhysChem*, 2023, 24 (15), pp.e202300182 (6). 10.1002/cphc.202300182. hal-04238212

HAL Id: hal-04238212

<https://hal.science/hal-04238212v1>

Submitted on 12 Oct 2023

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DOI: 10.1002/cphc.202300182

Research Article

Received: 22.March 2023

Revised: 18.April 2023

Accepted Article published: 12.May 2023

Dissociation of N₂ on a Si(111)-7x7 Surface at Room Temperature

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[**] A previous version of this manuscript has been deposited on a preprint server (DOI: <https://dx.doi.org/10.26434/chemrxiv-2022-rjcvc>)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cphc.202300182>

The dissociation of N₂ is successfully achieved at very low pressure and at room temperature on the Si(111)-7x7 surface. The dissociation of N₂ was investigated by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations.

scanning	tunneling	microscopy
nitrogen		activation
silicon		
STM		
XPS		

We demonstrate that the strong N₂ bond can be efficiently dissociated at low pressure and ambient temperature on a Si(111)-7x7 surface. The reaction was experimentally investigated by scanning tunnelling microscopy and X-ray photoemission spectroscopy. Experimental and density functional theory results suggest that relatively low thermal energy collision of N₂ with the surface can facilitate electron transfer from the Si(111)-7x7 surface to the π*-antibonding orbitals of N₂ that significantly weaken the N₂ bond. This activated N₂ triple bond dissociation on the surface leads to the formation of a Si₃N interface.

Introduction

Nitrogen (N₂) is an abundant diatomic molecule that makes up 78% of the atmosphere on Earth. It is therefore highly desirable to incorporate this typically inert molecule into the synthesis of value-added products or to use it as a reservoir of chemical energy.^[1] Industrially, atmospheric nitrogen enters the synthetic cycle through the well-established Haber-Bosch process, in which N₂ is hydrogenated to ammonia at high temperature (500°C) and pressure (200 atm).^[2] The extreme reaction conditions required for such an important economical process have significant energy implications, consuming approximately 1% of the world's

energy supply, mostly in the form of polluting coal.^[2c] Indeed, the thermodynamic stability of the N₂ molecule makes its use dependent on overcoming significant energy barriers and requires an activation step to cleave the N≡C≡N bond. Therefore, much work has been performed to increase the efficiency of the dissociation of N≡C≡N bond, mostly by using heterogeneous catalysts, such as reactive metallic surfaces.^[3,4] Dissociation of N₂ molecules is usually carried out at high temperature and high pressure because N₂ molecules interact weakly with most surfaces below room temperature (RT) and remain physisorbed (i.e., non-dissociated). The development of new strategies to dissociate the N₂ molecule under mild conditions is of primary interest. Molecule-surface collisions represent an interesting alternative because these collisional processes induce mechano-chemical or electron-transfer reactions that promote the dissociation of the reactants at low pressure and low temperature.^[5] The conversion of kinetic energy into vibrational excitation following the collision of molecules with a surface has been investigated mainly for hydrocarbon-based species,^[5a,5b] although a few examples of the dissociation of N₂ using a supersonic molecular beam to overcome the dissociation barrier via a hyperthermal collision have also been studied on metal surfaces.^[5,e,5f] These vibrational excitations can lead to dissociative states of the incident molecules, and result in the adsorption of dissociated fragments. One of the main interests of this mechanochemical reactivity is to perform it at low pressure, typically in ultra-high vacuum, which allows the use of scanning probe microscopies to identify the adsorbed products resulting from the collisions. In the case of electron transfer induced by molecular collision, a recent study showed that the C≡C=O bond in CO₂ molecules can be cleaved by a nonuniform charge transfer from the substrate to the CO₂ molecule due to the conversion of the kinetic energy of the incident CO₂ molecule into molecular deformation.^[5i] However, no studies have been reported for the dissociation of inert molecules such as N₂ using a similar activated electron-transfer mechanism on non-metallic surfaces. Here, we demonstrate that the dissociation of N₂ is successfully achieved at very low pressure and at room temperature on the Si(111)-7x7 surface. The dissociation of N₂ was

investigated by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. This is the first report demonstrating that the Si(111)-7x7 surface can be used for the dissociation of inert molecules, paving the way for the development of new surface chemistry.

Results and Discussion

The choice of the surface plays a crucial role in the search for an efficient approach to dissociate inert molecule such as N₂. Therefore, we chose the Si(111)-7x7 surface because this surface is known to be very reactive^[6] and is able to convert, for instance NO to N₂O by heterogeneous on-surface process^[6] or to dissociate NH₃.^[7] However, there are no reports on the dissociation of N₂ on the Si(111)-7x7 surface. After the preparation of the Si(111)-7x7 surface in ultra-high vacuum (UHV) by standard procedure, the surface was exposed to N₂ molecular gas for 30 minutes at different pressures ranging from 6×10^{-9} mbar to 5×10^{-5} mbar.

For pressures below 1×10^{-6} mbar, the surface STM images of the Si(111)-7x7 are unchanged compared to the initial clean surface (Figure¹a). Surprisingly, after exposure to N₂ gas at a pressure of 3×10^{-6} mbar for 30 min, unusual dark spots are observed in the STM images (Figure¹b). The density of these dark spots strongly increases after exposure at a pressure of 1×10^{-5} mbar, which corresponds to an exposure of about 24000 L of N₂ molecules (Figure¹c). Closer inspection of the STM image corresponding to an area of 15×15 nm² (Figure¹d) reveals that darker protrusions can be assigned to silicon adatoms in both faulted and unfaulted half-unit cells. In addition, STM images recorded for negative polarities (i.e., filled states) show that some rest-atoms appear as dark protrusions (Figure^{S1}). In order to detect a possible contribution from dissociated nitrogen, which may be generated by the filament gauge used to measure the pressure in the UHV chamber, N₂ exposure was performed on a clean Si(111)-7x7

surface while the gauge filament was turned off after reaching the deposition pressure (5×10^{-6} mbar). To investigate the influence of light excitation on the Si(111)-7x7 substrate, an additional test was performed with all chamber windows covered with aluminum foil to ensure complete darkness inside the chamber during the gas exposure. The gas line used to introduce N₂ gas into the UHV chamber was flushed and baked several times to eliminate any possible source of contamination. In both cases, the same amount of dark spots were observed on the Si(111)-7x7 surface, supporting the idea that there is no effect of the gauge filament or ambient light on the dissociation reaction.

In the following section, we have focused on describing the experimental data on the evolution of silicon adatoms, since the detection of more reactive silicon rest-atoms in STM images is too delicate to be rigorously included in the statistical analysis. To determine the evolution of extinct silicon adatoms as a function of N₂ pressure, we analyzed more than 50 STM images recorded at positive sample voltage (empty states) with different pressures but by keeping the exposure time to 30 minutes. The number of extinct adatoms in each STM image was determined by using the particle detection module included in the SPIP software[®].

The increasing number of dark protrusions as a function of N₂ pressure for a 30 min exposure at RT clearly shows a threshold at $P = 1 \times 10^{-6}$ mbar and a plateau when $1 \times 10^{-5} < P < 5 \times 10^{-5}$ mbar (Figure²). After exposure to N₂, the surface of Si(111) was then heated at 800 K for 30 min. No modifications were observed in the resulting STM images, recorded at both polarities (Figure^{S2}).

Then, we have investigated the evolution of extinct adatoms as a function of exposure time for a fixed pressure of 5×10^{-6} mbar of N₂ (Figure^{S3}). The number of extinct Si adatoms increases progressively with the duration of exposure to N₂. From the experimental data points, the plot of 1/(number of extinct Si adatoms) versus the duration of exposure to N₂ at a given pressure is a straight line (Figure^{S3b}), supporting a partial second order kinetic

law. Finally, we investigated the role of temperature. The STM images in Figure^{S4} compare the number of extinct adatoms of a Si(111)-7x7 surface exposed to 3×10^{-6} mbar of N₂ for 20 minutes at 120 K (Figure^{S4a}) and 300 K (Figure^{S4b}). The number of extinct silicon adatoms decreases sharply from 36% to 4.5% as the temperature increases from 120 K to 300 K. The number of extinct silicon adatoms increases with the N₂ pressure and exposure time, but decreases with the temperature of the substrate.

To understand the exact nature of the molecular changes due to the exposure of the N₂ molecule of the Si(111)-7x7 surface, we have used the XPS technique to provide elemental selective information in a second UHV setup including an STM and an XPS technique.

After exposure to N₂ (RT, 30 min, $P=2 \times 10^{-5}$ mbar), the modified Si(111)-7x7 surface was carefully examined by STM. In this second setup, the number of extinct adatoms is still equal to 0.35, as previously observed in the first STM setup. The XPS experiments show an N(1s) line in addition to the two Si(2s) and Si(2p) lines originating from the Si(111)-7x7 surface (Figure^{S5}). The N(1s) line is broad and asymmetric, as expected for a multicomponent line containing at least two species. The full width at half maximum (FWHM) of this line is approximately 2.2 eV. This peak was fitted to three components with binding energies (BE) of 400.1 ± 0.1 eV (A1, blue line), 398.6 ± 0.1 eV (A2, green line) and 397.6 ± 0.1 eV (A3, red line), respectively (Figure³a). Each component (A1, A2 and A3) was fitted with an FWHM value of 1.6 eV. Furthermore, the Si(111)-7x7 surface exposed to N₂ pressure ($P=2 \times 10^{-5}$ mbar, 30 min) was annealed at 800 K for 30 min. After this thermal annealing, the N(1s) line is sharper and consists of a single line with a BE of 397.6 eV. Its FWHM is found to be 1.5 eV. This value is consistent with that obtained for the three components of the N(1s) line before annealing (Figure³b). Note that the area of the N(1s) lines before and after annealing is almost the same (within a few percent). Therefore, this result clearly indicates that the nitrogen species, adsorbed on Si(111)-7x7 after

exposure at room temperature, are not desorbed after annealing at 800 K. The A1 and A2 lines (Figure 3a) observed before annealing correspond to intermediate species of partially dissociated N₂ molecules grafted on the Si(111)-7x7 surface.^[8] The main line before annealing (A3, Figure 3a) and the single line measured after annealing (Figure 3b), both located at a BE of 397.6 eV correspond to atomic N triply coordinated with silicon adatoms, i.e. Si₃-N, in which each N₂ molecule is completely dissociated into two nitrogen atoms bound to the surface.^[9] Thus, the extinct silicon adatoms observed in the STM images are attributed to silicon adatoms covalently bonded to nitrogen atoms. This result is also supported by the partial second order with respect to surface-adsorption sites discussed above (Figure 3). In addition, we have carefully checked the composition of the N₂ gas used in the experiment. The data sheet of the N₂ gas (6N, Linde gas) indicates that the gas contains nitrogen (99.9999%) with 1 ppm of impurities (reported as <0.5 ppm of H₂O, <0.5 ppm of O₂, <0.5 ppm of H₂, <0.1 ppm of CO, <0.1 ppm of CO₂, and <0.1 ppm of C_nH_m). The data sheet shows that there are no impurities containing nitrogen atoms (e.g. NH₃ or NO) in this type of N₂ gas. Therefore, the N(1s) line observed in the XPS spectra can only come from the N₂ molecules.

All experimental data, including atomic resolution STM images and XPS spectra, indicate that adsorbed N₂ molecules dissociate on the Si(111)-7x7 surface at room temperature after exposure to N₂ pressure higher than 1 × 10⁻⁶ mbar for 30 min. To support our experimental results, we have evaluated the adsorption energy and the electronic structure of the N₂ molecule at different adsorption sites of a Si(111)-7x7 surface with DFT calculations. We considered both “end-on” and “side-on” adsorption sites over a Si adatom and a rest-atom (Figure 4a). These four conformations have been previously identified as the most favorable adsorption geometries for N₂ on the SiC(111) surface.^[10] In contrast to the SiC(111) surface, our DFT results indicate that N₂ is weakly bound to the Si(111)-7x7 surface (E_{ads} ~ 0.3 to 0.6 eV, Table S1) with relatively long Si-C-N equilibrium distances (d_{Si-C-N} ~ 0.19 to

0.23^{nm}, Table^{S1}), reminiscent of a physisorbed state. For the end-on and side-on sites above a Si adatom, the geometry optimization leads to a similar structure where N₂ is tilted between a Si rest-atom and a Si adatom (Figure⁴_a). The corresponding equilibrium distance of N₂ on the Si(111)-7x7 surface is $d(\text{Si}-\text{N})=0.27^{\text{nm}}$ (Table^{S1}) and the adsorption energy is 0.33^{eV}. For the adsorption of N₂ over the rest-atom of Si, the orientation of N₂ is conserved in the two adsorption sites, end-on and side-on, but with a respective equilibrium Si-C-N distance of 0.19^{nm} and 0.23^{nm}. The corresponding adsorption energies are 0.49^{eV} for the end-on site and 0.60^{eV} for the side-on site. Finally, the structure of the Si(111)-7x7 surface is quite robust and remains weakly perturbed by N₂ adsorption. These DFT results confirm that Si rest-atoms are more reactive than adatoms.

In terms of electronic properties, the projected density of states (PDOS) of N₂ adsorbed on the Si adatom (green line) and on the Si rest-atom in an end-on (blue line) and a side-on (red line) geometry on the Si(111)-7x7 surface are plotted in Figure⁴_b with respect to the Fermi level of each system. The DOS of the gas phase N₂ molecule (black dashed line) is also shown for reference, with respect to the Fermi level of Si(111)-7x7. The PDOS clearly indicate that the energy of the lowest π^* -antibonding level of the gas phase N₂, centered at ~3.1^{eV} above the Fermi level, is drastically affected by the adsorption site. For all adsorption sites considered, this low-lying N₂(π^*) state is strongly shifted toward the Fermi level, and becomes partially occupied (see inset in Figure⁴_b). The two cases where N₂ is adsorbed in a side-on fashion (over a rest-atom or an adatom) show the larger overlap between the π^* state of N₂ and the surface Si atoms. Charge distribution analysis using the Bader approach^[11] reveals a real charge transfer from Si(111)-7x7 to N₂, and the magnitude of the charge transfer increases as the Si-C-N distance decreases (see Table^{S1}).

Therefore, an increase in pressure should increase the absolute number (but not the fraction) of N₂ molecules colliding with the surface, including an increase in the number with

sufficient kinetic energy to bring N_2 closer to the Si(111)- 7×7 surface, ultimately improving the partial occupation of the π^* states of N_2 to facilitate the breaking of the $N\langle C=3\rangle N$ bond. Consistent with such a description, DFT calculations reveal a significant charge transfer towards N_2 at 0^{K} , then one can easily expect that an increase in temperature will improve such a charge transfer. Indeed, as the PDOS of the π^* -antibonding level moves below the Fermi level, the partial electron transfer from the Si(111)- 7×7 surface to the lowest π^* -antibonding states of N_2 improves. As observed in the XPS spectra (see Figure³[<xfigr3>a](#)), such electron transfer to the N_2 - π^* state favors a subsequent spontaneous $N\langle C=3\rangle N$ partial bond cleavage at the interface. Thermal annealing at 800^{K} then leads to the complete dissociation of any remaining $N\langle C=3\rangle N$ bonds, yielding atomic N triply coordinated with silicon adatoms. This electron transfer, which occurs even at low temperatures, is the main driving force of the N_2 dissociation process.^[10] Indeed, the occupation of the lowest π^* -antibonding orbital of N_2 already occurs when N_2 is physisorbed, and this could be enhanced during N_2 collision with the surface when the distance of the N_2 -Si(111)- 7×7 surface becomes smaller than in the physisorbed phase. The charge transfer into the N_2 - π^* state is larger for molecules with a side-on or a tilted orientation because the overlap between the N_2 - π^* and Si states is larger than in the case of the end-on orientation (see inset, Figure⁴[<xfigr4>b](#)). Finally, we observed a decrease in the number of extinct silicon adatoms with increasing temperature (Figure^{S4}), we can conclude that the process of dissociation is called a “facile system”.^[5i,5j] This is also consistent with our DFT results indicating that N_2 is physisorbed on Si(111)- 7×7 ; low temperature conditions should improve the “sticking” of N_2 to the Si(111)- 7×7 surface.

Conclusion

In conclusion, we have successfully demonstrated that N_2 dissociation can be achieved at low pressure and ambient temperature on a Si(111)- 7×7 surface. Our results suggest that electron-transfer from Si(111)- 7×7 surface to the π^* -states of N_2 ultimately weakens the $N\langle C-$

>N bond. This leads to cleavage of the N₂ triple bond at the surface, resulting in the formation of a Si₃N interface. Our results provide a better understanding of the growth of silicon nitride precursors, which is extremely important for microelectronics applications.^[12] In addition, the possibility of ammonia synthesis using a Si(111)-7x7 surface is currently being investigated.

Experimental Section

Preparation of the Si(111)-7x7 Surface

A Si(111) substrate n-doped with phosphorus (0.001--0.002^Ωcm) mounted on a molybdenum sample holder is used to prepare the Si(111)-7x7 surface. Under UHV, the sample was then degassed to 800[°]C by direct current heating while maintaining the pressure in the chamber below 3×10⁻⁹ mbar. The sample was then flashed several times at 1200[°]C until this temperature could be maintained for 10^s without exceeding the 10⁻¹⁰ mbar pressure range. After each flash-cycle, we allowed the time for the pressure to normalize before proceeding to the next flash. After the last flash, the temperature was immediately lowered to approximately 950[°]C and then gradually lowered at a rate of 10[°]C/min to 750[°]C. Below 750[°]C, we quickly cut the current and allowed the sample to cool. Since we use a pyrometer to control the sample temperature, this method ensures that the sample is exposed to 850[°]C, where the Si(111)-7x7 surface reconstruction occurs. The sample was then transferred to the STM head and scanned to check the state of the surface and its cleanliness.

N₂ Gas and Method for Its Deposition

Scientific grade molecular N₂ gas of 99.9999% purity, purchased from Linde Gas, was used in this work. In addition, the gas line that carries the gas from the pressurized bottle to the chamber was pumped and baked until the achievement of a UHV condition similar to that in the preparation chamber was achieved with a measured base pressure equal to 6.7×10⁻¹¹ mbar. After scanning and approving the surface cleanliness, the Si(111)-7x7 sample was placed on the manipulator and held at RT in front of the capillary tube of N₂ gas injection. The distance between the sample surface and the end of the

capillary tube is about 15^{cm}. The gas flow is controlled by a high-precision leakage valve and by following the pressure measured inside the preparation chamber with a filament gauge. This sample exposure to gas is known as the “bulb” method, where the flux of molecules is contained with a thermal distribution of the kinetic energies following the law of the Maxwell-Boltzmann distribution.

X-ray Photoelectron

X-ray photoelectron experiments were performed with a hemispherical analyzer Omicron EA¹²⁵ equipped with a dual anode X-ray source (Omicron, DAR 400) using Al K α X-ray source ($h\nu=1486.6$ eV) radiation. The photoelectrons were collected at normal electron emission. The angle of acceptance of the photoelectron analyzer was set to $\pm 1^\circ$. The spectrometer energy scale was calibrated to the Ag 3d_{5/2} core level line measured on a clean Ag sample, set at a binding energy of 386.25 eV. The Si(111) sample is still conductive after N₂ adsorption and this procedure guarantees a good estimation of the N(1s) lines binding energy. The spectra were recorded using a pass energy of 20 eV for high resolution and 50 eV for a wide scan. The peak was fitted to mixed Gaussian-Lorentzian components using XPS-CASA software.^[13] after subtracting a Shirley-type background.

Density Functional Theory (DFT)

Density Functional Theory (DFT) calculations were carried out at T=0 K with Siesta package^[14] (version 4.1.5) and the results were visualized with the Chimera software.^[15] We used periodic boundary conditions with the well-known PBE functional in conjunction with the semi-classical van der Waals corrections developed by Grimme.^[16] The computations were performed with norm-conserving Trouillier-Martins pseudopotentials and double- ζ polarized atomic basis sets. The mesh cut-off used to form the real space grid in the DFT calculations was 500 Ry, and the structural relaxation and geometry optimization were carried out using conjugate-gradient method until the forces and the variation of total energy were less than 0.01 eV/Å and 0.0001 eV, respectively. We considered a vacuum region of 35 Å to minimize the interactions between periodic images in the

direction normal to the slab. The adsorbed N₂ molecule in the supercell was fully optimized as well as the first three upper layers (of the seven layers model), while the remaining four deeper layers of the Si(111)-7x7 surface slab model (298 Si atoms) were fixed at the optimized geometry of pristine Si(111)-7x7. The bottom layer of this Si model was saturated with hydrogen (49 H atoms) to avoid the effect of Si dangling bonds. All optimizations were performed at Γ -point (k-point mesh of 1×1×1), and all the properties were obtained with a 9×9×1 k-point grid. A Bader charge analysis was performed with the Bader code developed by the Henkelman group.^[11]

Acknowledgements

The authors acknowledge the financial support of the <cgs>French National Research Agency</cgs> through contract OVATION (<cgn>ANR-19-CE09-0020</cgn>) and from the <cgs>Pays de Montbéliard Agglomération</cgs>. A.R. and N.B. acknowledge the support of the <cgs>Natural Sciences and Engineering Research Council of Canada (NSERC)</cgs>, and they are grateful to Calcul Québec and Compute Canada for providing computational resources.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Figure¹ STM images of the Si(111)-7x7 surface after an exposition to N₂ at 300^K for 30 minutes. STM images were recorded (50×50^{nm}², I_t=200^{pA}, V_s=+2^V) upon exposure at a pressure of a) 1^{M.}×10^{M->6}^{mbar} (here, the black spots are mainly attributed to defects originating from the initial surface preparation), b) 3^{M.}×10^{M->6}^{mbar} and c) 1^{M.}×10^{M->5}^{mbar}. The increasing number of unusual darker protrusions in b) and c) originates from the interaction of N₂ with the surface. d) STM image (15×15^{nm}², I_t=200^{pA}, V_s=+1.5^V) recorded after exposure at 1^{M.}×10^{M->5}^{mbar} for 30 minutes. Darker spots are attributed to modified silicon adatoms, both adatoms of faulted (yellow triangle) or unfaulted (black triangle) half-unit cells are affected.

Figure² Evolution of the number of extinct silicon adatoms after the exposition of Si(111)-7x7 surface at RT during 30 minutes to a pressure of N₂ gas varying from 1^{M.}×10^{M->7}^{mbar} to 5^{M.}×10^{M->5}^{mbar}. The experimental data (black circle) are fitted numerically by a sigmoid function (red line).

Figure³ a) N(1s) core level spectrum after exposition of the Si(111)-7x7 surface to N₂ molecules (RT, 30 minutes, P=2^{M.}×10^{M->5}^{mbar}). The experimental data (black dots) with a FWHM of 2.2^{eV} are fitted with three components with binding energies of 400.1±0.1^{eV} (A1, blue line), 398.6±0.1^{eV} (A2, green line), and 397.6±0.1^{eV} (A3, red line), each corresponding to chemically inequivalent N atoms. b) N(1s) core level spectrum recorded after thermal annealing at 800^K for 30 minutes of the sample analyzed in a). The experimental data (black dots) are fitted with a single binding energy of 397.6^{eV} (blue line), corresponding to a single type of N atoms.

Figure⁴ a) Identification of the most reactive adsorption sites on the Si(111)-7x7 surface. The Si adatoms (in red) and rest-atoms (in green) of the topmost layers in the faulted (F) region of the unit cell used in the DFT calculations are identified in the left side models. The black circles are the adsorption site considered. The optimized end-on and side-on adsorption

geometries on Si rest-atom are shown in the middle, and the optimized tilted geometry obtained for adsorption on Si adatom is reported on the right image. b) Projected DOS of a N_2 molecule in the gas phase (black dashed line), and at equilibrium between a Si rest-atom and a Si adatom into a tilted geometry (green line), and over a rest-atom into an end-on (blue line) and side-on (green line) geometry with respect to the calculated Fermi level (E_F). A zoom of the different $N_2(\pi^*)$ -Si overlaps around E_F is shown in the inset. White: Hydrogen atoms, light brown: Silicon atoms, and blue: Nitrogen atoms.