Evolution of CH_3NO_2/Si interfacial chemistry under reaction conditions: a combined experimental and theoretical study

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Supporting information

Sample preparation and instrumentation: An undoped Si (100) wafer was purchased from Sigma Aldrich, USA. It was cleaned using a few cycles of 1 keV Ar^+ bombardment, followed by annealing at 1150 K (15 min) for surface structure restoration. This pretreatment method led to a reconstructed Si(100)-2×1 surface.[1, 2] The cleanness of the Si substrate surface was checked using XPS. The *in situ* XPS study was performed over wide ranges of CH_3NO_2 vapor pressures (10^{-10} - 5 mbar) and surface temperatures (298-773 K). CH_3NO_2 purchased from TCI, America was freeze-pump-thawed several times to remove gaseous contaminants prior to the introduction of vapor into a reaction cell.

All experiments were performed using the APXPS system in the Notre Dame Radiation Laboratory. The photoemission spectra were obtained with a SPECS Phoibos 150 Hemispherical Energy Analyzer that was coupled to a differential pumping electrostatic lens system. A micro-focus X-ray (XR-MF) source produced Al Kα X-rays (1486.7 eV). The X-rays were monochromatized and then transmitted through a silicon nitride membrane of the reaction cell installed in an analysis chamber. The reaction cell was custom designed to perform surface

characterization at elevated pressures (up to 25 mbar) and temperatures (up to 873 K). Detailed descriptions of the experimental instrumentation have been provided in our previously published work.[3, 4] At each experimental condition, a stabilization time of 20 min was allowed before recording any photoemission spectra. The binding energy scale was calibrated using the bulk Si $2p_{3/2}$ at 99.2 eV as a reference.[5] Representative N 1s photoemission spectrum recorded after the evacuation of 5 mbar of CH_3NO_2 at room temperature (RT) is shown in Fig. S1. Photoemission spectra of C 1s and N 1s obtained under various pressures of CH_3NO_2 at RT are shown in Fig. S2.

Control experiments: The clean Au substrate was free of carbon and oxygen contaminants under UHV conditions (Fig. S3). Upon the introduction of CH_3NO_2 vapor, a small amount of molecular adsorption of CH_3NO_2 onto the Au surface was observed. However, the contribution of molecular CH_3NO_2 was totally quenched due to evaporation at elevated temperatures (Fig. S3). Except for a gas-phase CH_3NO_2 signal, no N 1s, C 1s, or O 1s was detected on the Au surface at 573 K (Fig. S3).

Low energy electrons: It has been reported that CH_3NO_2 can be affected by a dissociative electron attachment (DEA) process when incident electrons have energy as low as a few eV.[37,6, 7] Therefore, there was a possibility that dissociation of the C-N bonds could be caused by the outgoing photoelectrons in our experimental conditions. We recorded the spectra of low energy photoelectrons at both the CH_3NO_2/Si(100)-2×1 (Fig. S4a) and CH_3NO_2/Au (Fig. S4b) interfaces under various experimental conditions. We did not observe any C-N bond damage in the CH_3NO_2/Si(100)-2×1 or CH_3NO_2/Au experiment. It is worth noting that the photoelectron densities in the AP-XPS experiment were below 500 counts per second, which is far less than the current density used in the DEA experiment ($\sim 5 \times 10^{10}$ to $\sim 1 \times 10^{12}$ electrons cm^{-2} s^{-1}).[6]

Theoretical simulations: DFT calculations were carried out using the generalized-gradient approximation (GGA) as revised Perdew-Burke-Ernzerhof (RPBE) for exchange-correlation potentials,[8] the projector augmented waves (PAW) method,[9, 10] and a plane-wave basis set of 450 eV, as implemented in the Vienna *ab initio* Simulation Package (VASP).[11, 12] Dispersion corrections, which takes van der Waals interactions into account, were made at the DFT-D2 level[13] and are known to provide a better description of geometries and corresponding energies than those from the standard DFT.[14, 15]

In this study, we used a slab model of seven layers of Si-atoms with the bottom layer saturated by 32 H-atoms ($Si_{112}H_{32}$) in a 4×4 supercell (15.47Å×15.47Å×38.20Å in size). The adsorbed molecule was put on the top surface of the slab. The surface Brillouin-zone was sampled using a 2×2×1 *k*-mesh. All atoms, except the bottom three layers of Si atoms, were fully relaxed until the net residual force on every atom is less than 0.02 eV/Å. The potential-energy profiles along the reaction pathways were revealed using the climbing image nudged elastic band (CI-NEB) technique.[16]

Figure S5 shows all 10 initially considered configurations for CH_3NO_2 adsorption onto a Si(100)-4×2 surface, and Figure S6 summarizes the entire reaction from CH_3NO_2 to dissociated O and N atoms and CH_3 group on the Si(100)-c(4×2) surface through an alternative pathway. Both the lower reaction barrier and the more stable final-states confirm that the pathway shown in Fig. 3 is energetically more favorable.

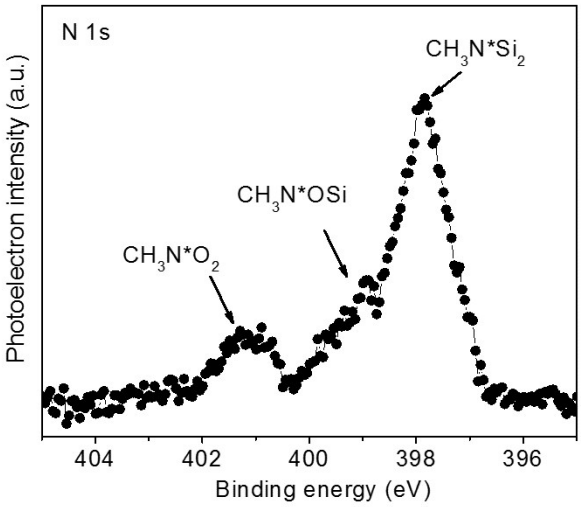

Fig. S1. *The photoemission spectra of N 1s obtained after the evacuation of 5 mbar of CH_3NO_2 at room temperature (RT) with assigned N-based species.*

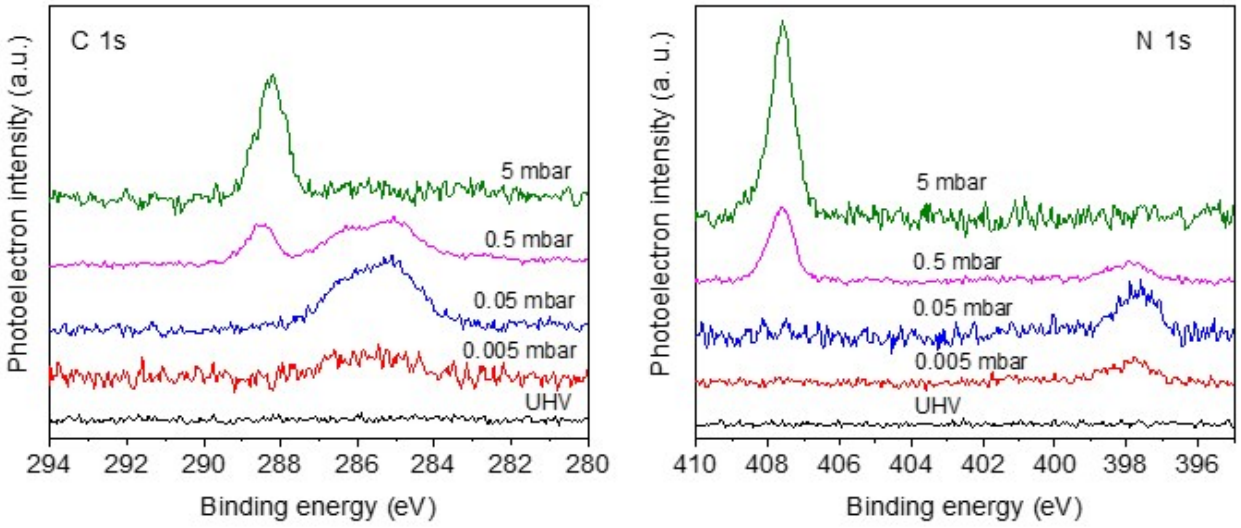

Fig. S2. *Photoemission spectra of C 1s and N 1s obtained under various pressures of CH_3NO_2 at RT.*

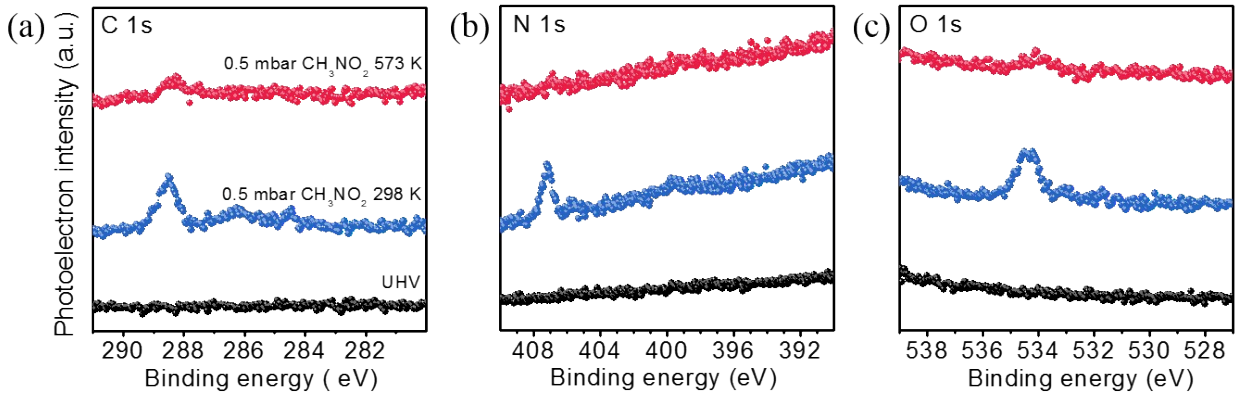

Fig. S3. *Photoemission spectra of C 1s, N 1s, and O 1s under three experimental conditions for CH_3NO_2 interaction with a clean Au substrate: UHV, 0.5 mbar CH_3NO_2 at RT, and 0.5 mbar CH_3NO_2 at 573 K.*

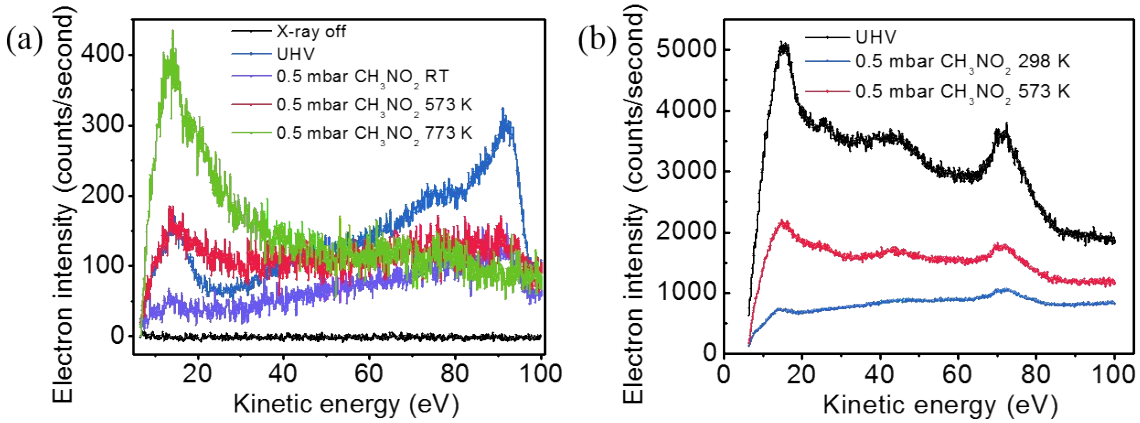

Fig. S4. *a) Low energy electron spectra obtained for Si (a) and Au (b) substrates under various conditions.*

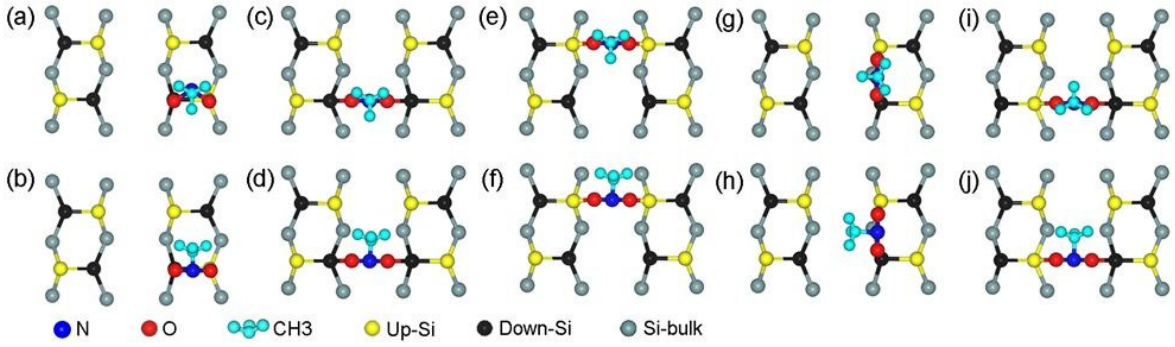

Fig. S5. *Panels (a) to (j) are all 10 initially considered configurations for CH_3NO_2 adsorption on a Si(100)-4×2 surface. Filled blue, red, cyan, yellow, black and gray balls represent N, O, CH_3, Up-Si, Down-Si, and Si-bulk atoms, respectively.*

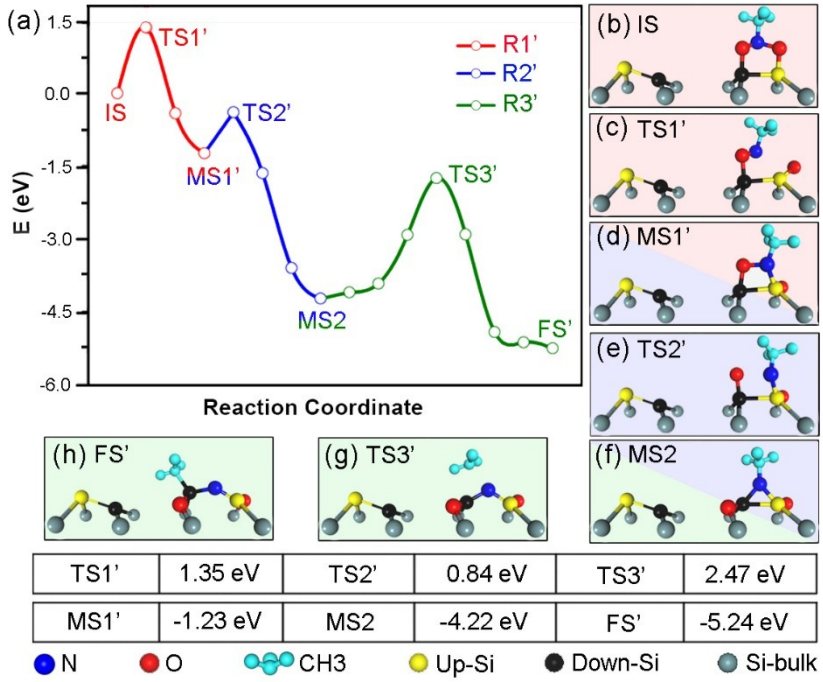

Fig. S6. *Reaction pathway for the dissociation of CH_3NO_2 on Si(100). Panel (a) is the energy profile for the three consecutive steps: R1' (red curve), R2' (blue curve), and R3' (green curve). The initials IS to FS' stand for initial-, transition-, metastable-, and final-states of the pathway. Their associated atomic structures were plotted in panels (b) to (h). Highlighted background colors denote the three reaction steps R1', R2', and R3' by light red, light blue and light green, respectively. Exact values of the reaction barriers and energies for MS1`, MS2 and FS`, in reference to that of IS, were listed in the table. Filled blue, red, cyan, yellow, black, and gray balls represent N, O, CH_3, Up-Si, Down-Si, and Si-bulk atoms, respectively. As mentioned in the main text, there are two possible pathways if the reaction proceeds from configuration MS2 to a final product. In MS2, the N atom bonds to the two Si atoms underneath it with equal bond lengths of 1.75 ± 0.01 Å. Figure 3 (f) to (h) shows one possibility for the CH_3 group to approach the Up-Si atom and the whole system reaches FS. In the alternative pathway (step R3'), the CH_3 group*

moves along the opposite direction and attaches to the Down-Si atom, as shown in Fig. S5(f) to (h), with a barrier of 2.47 eV that is 0.03 eV higher than that of step R3. A new final-state (FS') is shown in Fig. S5(h), which is 0.20 eV less stable than the FS in the original pathway. This energy difference lies in the fact that the Si-Si dimer underneath keeps its original buckled direction in FS, i.e. the position of Up-Si is vertically higher than that of the Down-Si. However, in FS', the attachment of the CH_3 group to the Down-Si inevitably flips the buckled direction, leading to a higher energy for FS'.[15]

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