

## Directed long-range molecular migration energized by surface reaction

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### 1. Introduction

#### 1.1. Molecular migration on a surface

- a phenomenon which is observed during the adsorption and the desorption of a molecule
- a fundamental step in many surface phenomena
- => self-assembly, material growth, phase separation, heterogeneous catalysis and molecular nanomachine<sup>1</sup>
- observation method: scanning tunneling microscopy (STM)<sup>2</sup>, ultrafast laser spectroscopy<sup>2</sup>

#### 1.2. Adsorption mode of molecule

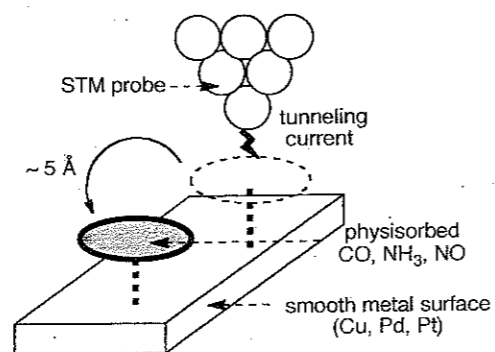
- physisorption : weak adsorption via van der Waals force between the molecule and surface
- chemisorption : strong adsorption via covalent bond with the dangling bond on the surface
- \* The adsorption and desorption of molecule are induced by physical stimuli such as electric, thermal and pressure.

#### 1.3. Previous work

- Molecular migration energized by electrostatic interaction<sup>2</sup> (Fig. 1)
- Migration range was very short ( $\sim 5 \text{ \AA}$ ).
- Direction of molecular migration was random.

Figure 1.

Migration of physisorbed molecule driven by electrostatic interaction.



#### 1.4. This work

- Discovery of a novel phenomenon; **directed long-range migration** of ethylenic products in the plane of Si(100) surface (Fig. 2)
- **Surface reaction** energized the molecular migration.
- Migration range was **much longer** ( $\sim 200 \text{ \AA}$ ) than that of previous work.
- It was observed that **clear direction** of molecular migration along the C–C bond axis in the initial chemisorbed state.

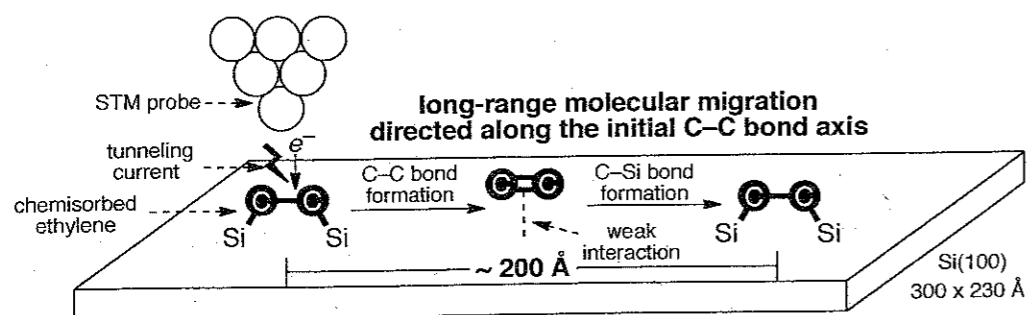


Figure 2. Migration of chemisorbed molecule energized by surface reaction on Si(100) surface.

## 2. Results and Discussion

### 2.1. Electron-induced reaction and migration of ethylene

- After injection of an electron pulse ( $-3 \text{ V}$ ,  $0.2 \text{ nA}$ ,  $0.5 \text{ s}$ ), the pulsed ethylene migrated (Fig. 3a).
- Migrated ethylene appeared predominantly as a parallel-adsorption form of chemisorbed product (in 90 %) (Fig. 3b).
- electron-induced events ( $N \approx 1,400$ ) at room-temperature
- the migration of ethylene (67 %)
- switching of the ethylene configuration from parallel-adsorption form to vertical-adsorption form without migration (28 %)
- Ethylene got out of measurement area. (5 %)
- A threshold of  $-3.0 \text{ V}$  of pulse bias is obtained assuming a linear threshold law (Fig. 3c).
- A linear relationship is observed, indicative of a single-electron process (Fig. 3d).

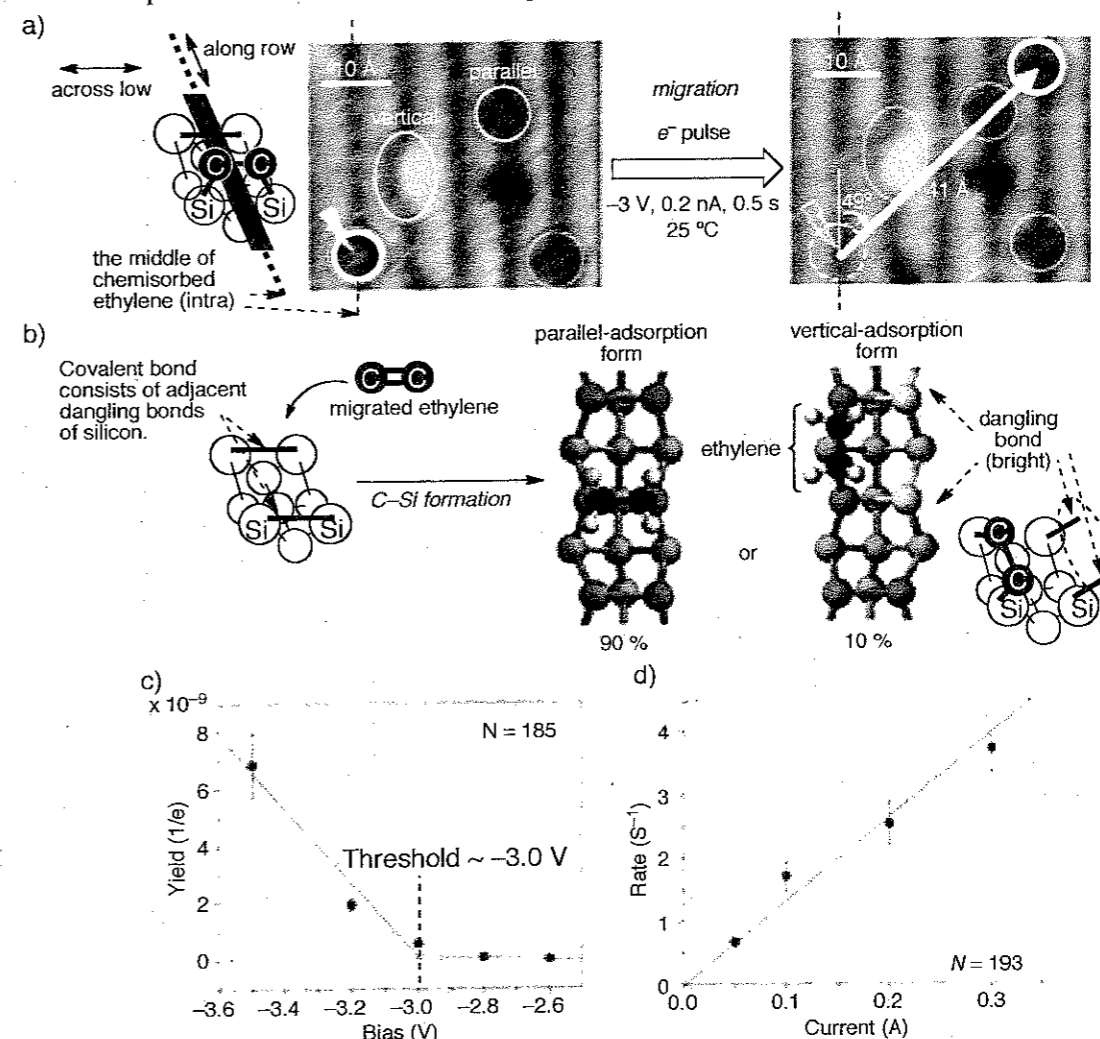


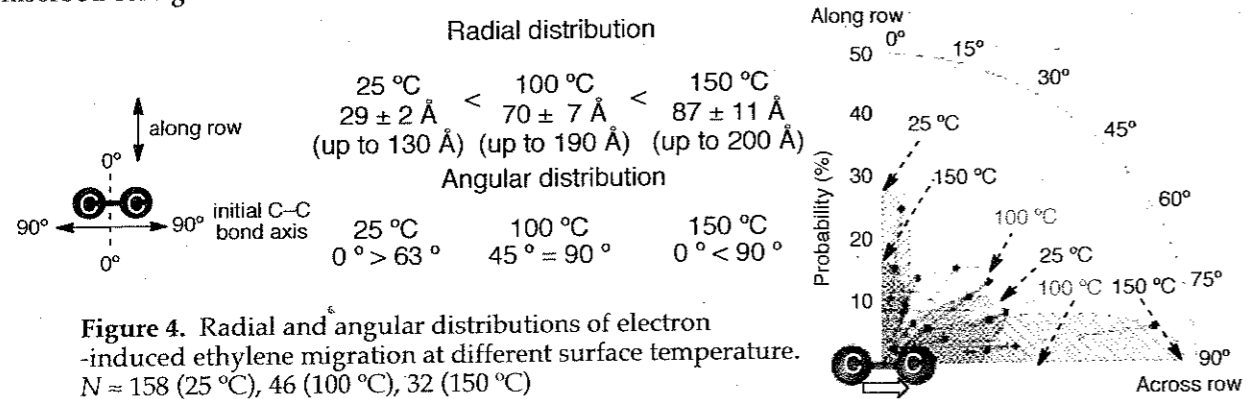
Figure 3. a) STM images ( $+2.0 \text{ V}$ ,  $0.2 \text{ nA}$ ,  $25 \text{ }^\circ\text{C}$ ), showing parallel-adsorption form (circle) and vertical-adsorption form (oval) of chemisorbed ethylene on Si(100). b) Schematics image of chemisorbed ethylene on Si(100). c, d) Yield and rate of electron-induced migration as a function of pulse bias and current.

#### < Radial and angular distributions of electron-induced ethylene migration >

- Characteristics of diffusion of chemisorbed ethylene from Si(100) **without** electron pulse
- Diffusion of chemisorbed ethylene is typically favored along the row (shown in figure 3a) because of the lower diffusion barrier than that of across row.<sup>3</sup>
- Chemisorbed ethylene desorbs from Si(100) at  $\sim 227 \text{ }^\circ\text{C}$ .<sup>4</sup>
- In this paper, the diffusion was not observed at room temperature.

- With electron pulse, as the surface temperature was raised, the radial distribution became broader and the average distance increased. At the same time, the angular distribution became sharper (Fig. 4).

=> On the hot surface, the ethylene migrated predominantly along the direction of the C-C bond of its initial chemisorbed configuration.



## 2.2. Electron-induced reaction and migration of propene

=> In order to obtain an evidence for directed long-range migration along the direction of the C-C bond axis of adsorbates

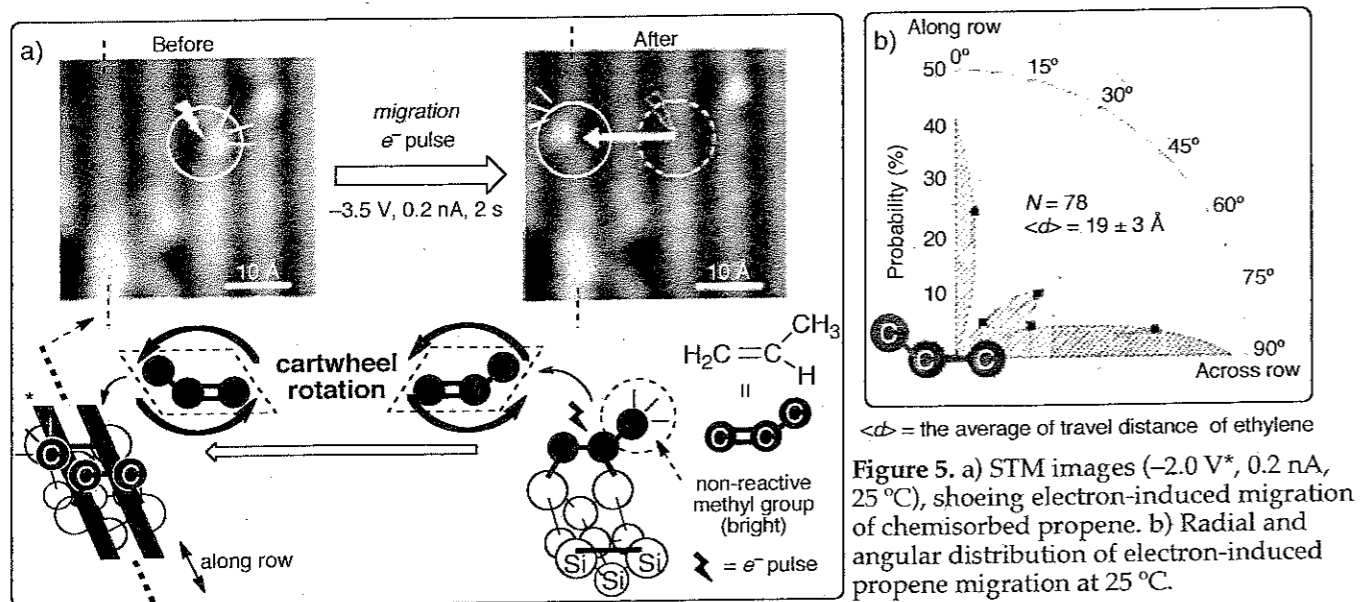
- In 70 % of cases of the migration of propene, the directionality of the migration along its bound C-C axis, away from the methyl group, was observed irrespective of which C-Si bond was pulsed (Fig. 5a).

=> The methyl group enhances electronic excitation at the neighbouring C-Si bond.

- In 62 % of cases, methyl group appeared at the opposite end of the molecule from its initial location after the migration (Fig 5a).

=> cartwheel rotation

- Shorter migration distance and higher trend in desorption along row of propene (Fig 5b) due to the increased number of degree of freedom in the chemisorbed propene and hence increased inelasticity of the chemisorbed propene



## 2.3. DFT calculation of electron-induced migration of ethylene and mechanism of migration

- Charge distribution in the first excited state shows asymmetric charge distribution. The higher charge density on one C-Si bond is accompanied by a larger repulsive force ( $0.17 \text{ eV \AA}^{-1}$ ) on the carbon atom (Fig. 6a).

=> creation of a net torque that could initiate motion along the direction of the C-C bond axis

- The cartwheel rotation of ethylene can be attributed to a torque arising from asymmetric forces on the carbon atoms during the release of ethylene (Fig. 6b step A).

- Highly rotationally excited molecules are unreactive (Fig. 6b step B).<sup>5</sup> Following rotational cooling in the course of migration, the ethylene adsorbs to the silicone surface (Fig. 6c step C).

=> The distance of migration depends on the rate of energy loss through transfer to the surface.

- According to the observed inversion of the propene molecule, the adsorbate travels in the direction with cartwheel rotation at a rate of approximately once per angstrom.

- They ruled out other mechanism of migration.

× Scattering of molecules from the STM tip or transfer of molecules to the tip => random event

× The electric field present in the STM junction as a source of migration => depends on the position of the STM tip

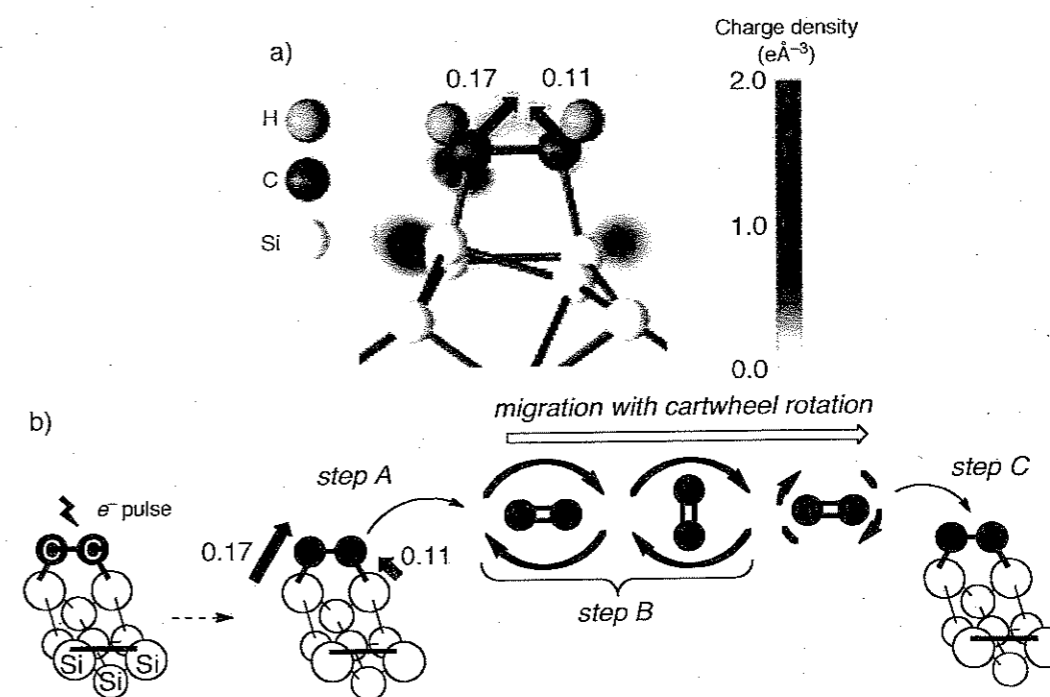


Figure 6. a) Calculated charge distribution in the first excited state of chemisorbed ethylene on Si(100) following a Frank-Condon transition. b) Schematic image of the mechanism of electron-induced migration.

## 3. Conclusions

A novel phenomenon; directed long-range migration of ethylenic products in the plane of the surface was reported.

- For electron-induced migration of ethylene, the migration is directed along the initial C-C bond axis in the chemisorbed state.

- The mechanism for the migration gives evidence of being rolling.

- The rotation is induced by torque.

## References

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