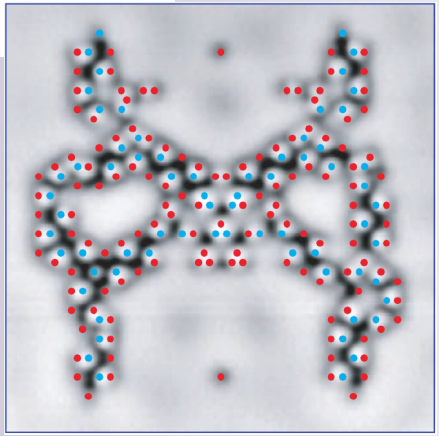
journal club presentation

by Lydia Nemec

Molecule Cascades
A. J. Heinrich, *et al.*
Science **298**, 1381 (2002);
DOI: 10.1126/science.1076768



Outline

- apparatus and methods
- configuration of CO molecules on a copper (111) surface

  ➡ **“molecule cascades”**
- stability of CO on Cu (111)
- toppling dominoes at nanometer-scale and low temperatures
- cascade logic circuits
- cascades and computation

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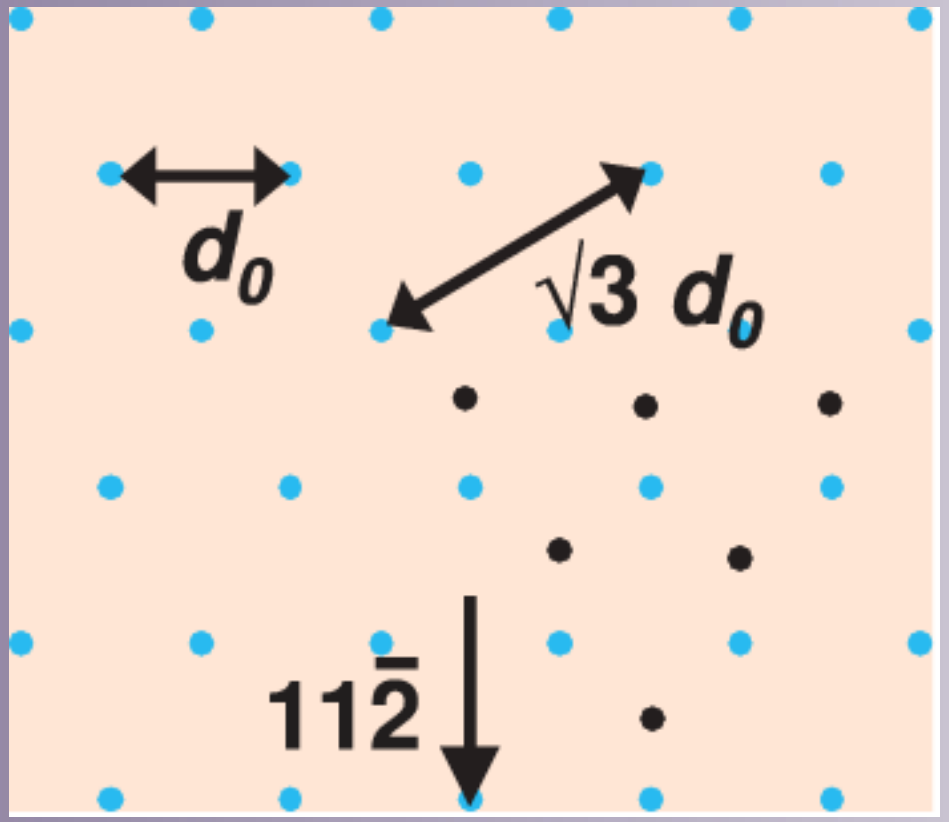
Apparatus and methods



- STM at low temperature and ultra-high-vacuum
  - fixed at 5K
  - variable between 0.5K and 40K
- clean Cu(111) single crystal surfaces

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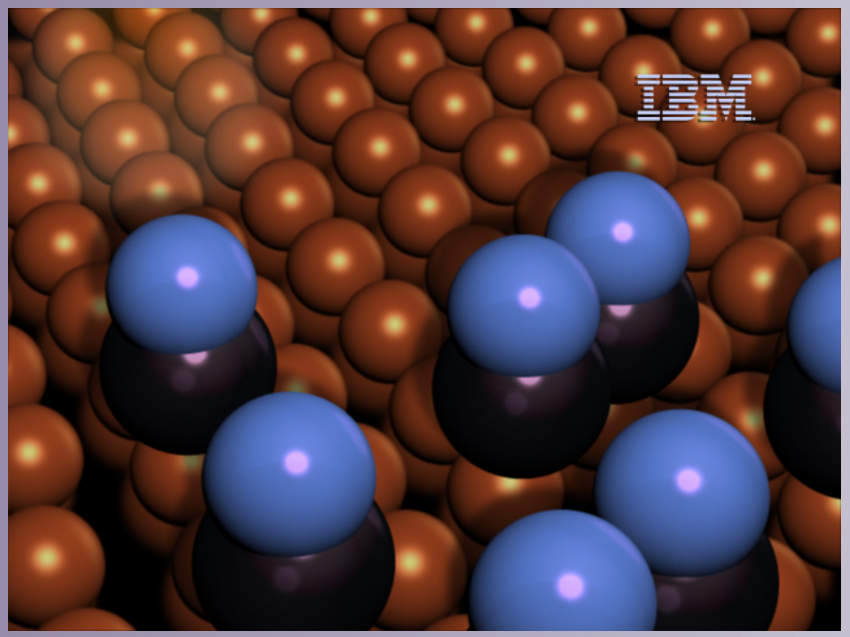
Apparatus and methods

Adsorbing CO molecules onto Cu surface



- admitting CO gas with the crystal held at 15 K
- CO binds on top of the surface Cu atoms standing upright with the carbon atom closest to the Cu surface

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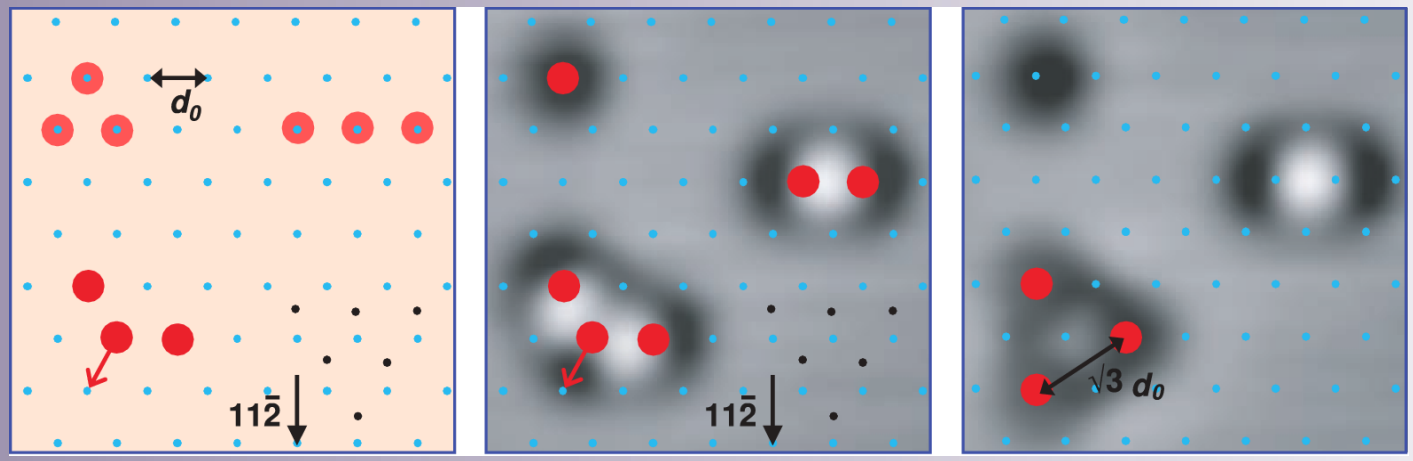
The stability of CO on Cu(111)

CO configurations



- CO monomer
- 2 CO as nearest neighbours “dimer”
- “trimers”: - 3-fold symmetric closed package
  - bend-line configuration
  - straight-line configuration

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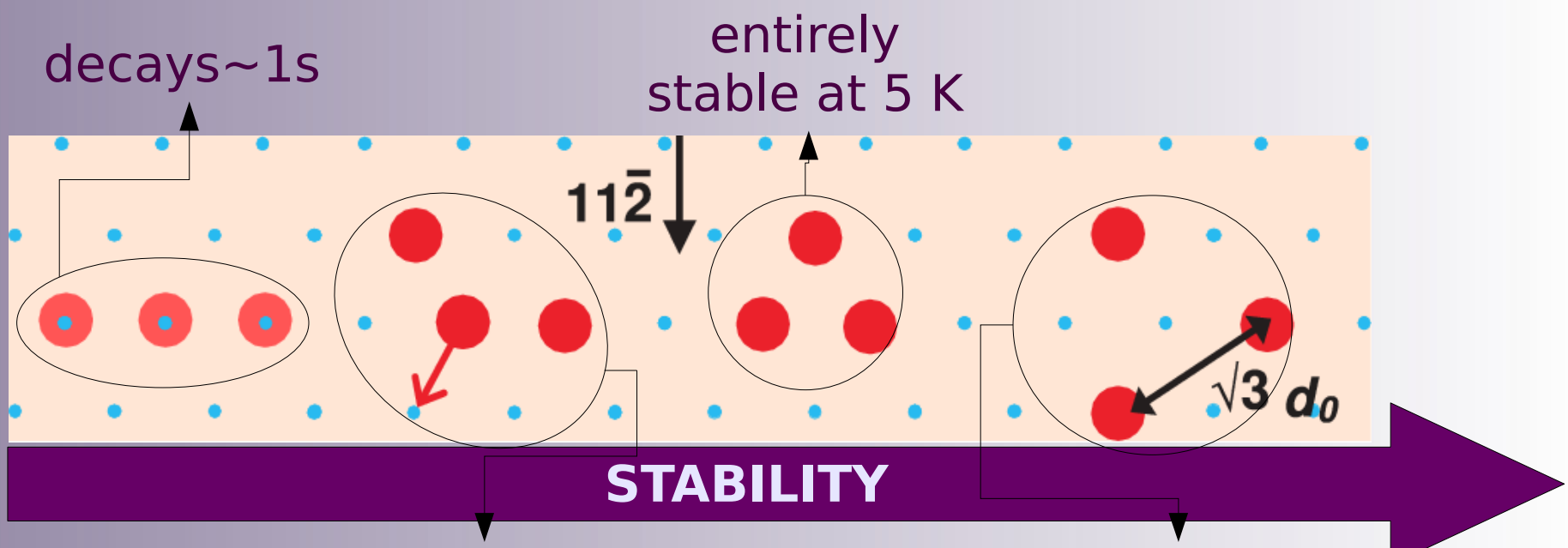
The stability of CO on Cu(111)



"chevron"
stable enough to
image
decays ~1min
decay only as shown

low-energy spacing,
island formation
observed at higher
temperatures (>5K)

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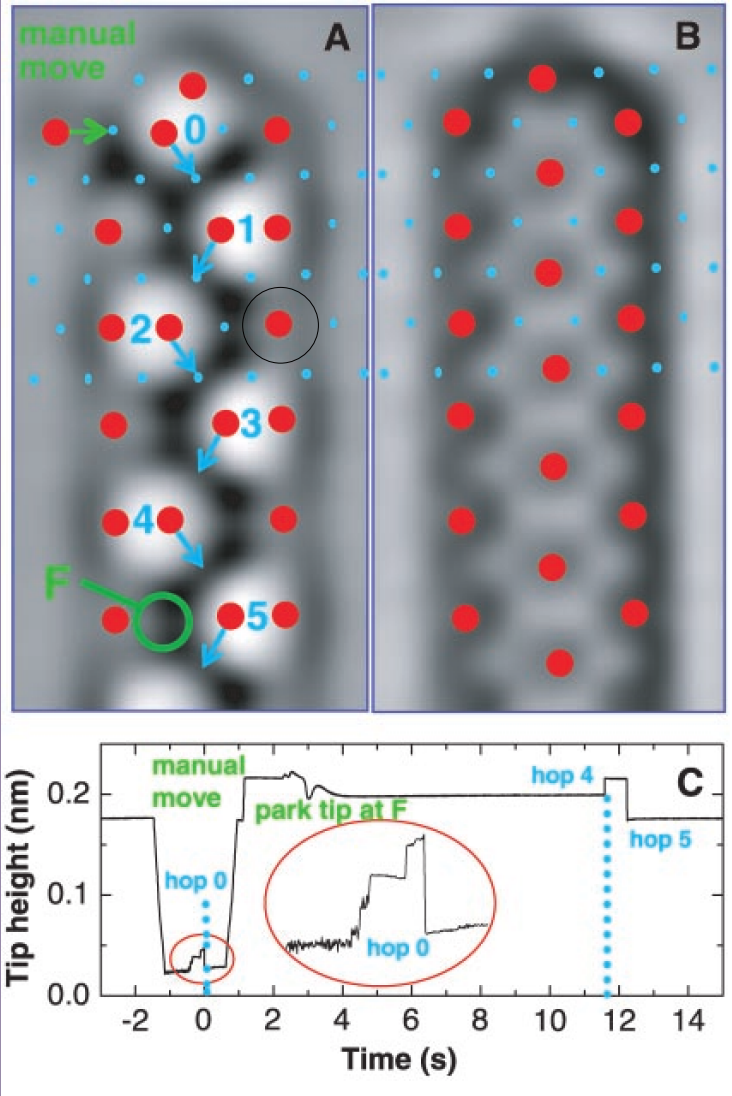
Molecule Cascades

Linked chevron cascade



- form an initial chevron
- chevron decays spontaneously

→ forms a new chevron

- energy of the system lowered with each hop
- If thermal energy is higher than the change in energy due to a hop, backwards hops became possible

→ propagation time rises

The hopping mechanism

environmental dependency

- presence of STM tip influences the decay rate
  (e.g. repeated imaging or holding the tip fixed)
- nearby defects (e.g. steps)

minimized proximity effects:

- STM tip only used to start the cascade and to detect a characteristic signal near the end
- enclosed cascades with CO walls

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The hopping mechanism

Model of the hopping rate

$$hopping\,rate[R] = \frac{(number\,of\,hops)}{(propagation\,time)}$$

$$R = R_{QT} + A \cdot e^{(\frac{-E}{Tk_B})}$$

R ... hopping rate
R_{QT} ... tunneling rate
E ... activation energy
A ... Arrhenius Factor

- in this case: tunneling from thermally excited states of the molecule

see

Understanding the Hopping Mechanism of Molecule Cascades at Very Low Temperatures
A.J. Heinrich, C.P. Lutz, J.A. Gupta, and D.M. Eigler
12th International Conf.
American Institute of Physics
2003 Volume 100 page 168-176

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Cascades logic circuits

Mechanical computation

- A molecule cascade serves as a wire to communicate 1 bit
- toppled and untoppled states representing binary 0 and 1
- different kinds of gates are possible
- difficulties with NOT gate
- NOT gate requires that all molecules in the output are untoppled, when the input topples
  → untoppled state has higher energy than toppled
- NOT gate can be realized in a 2-Input-Sorter (so-called “clocked-NOT”)

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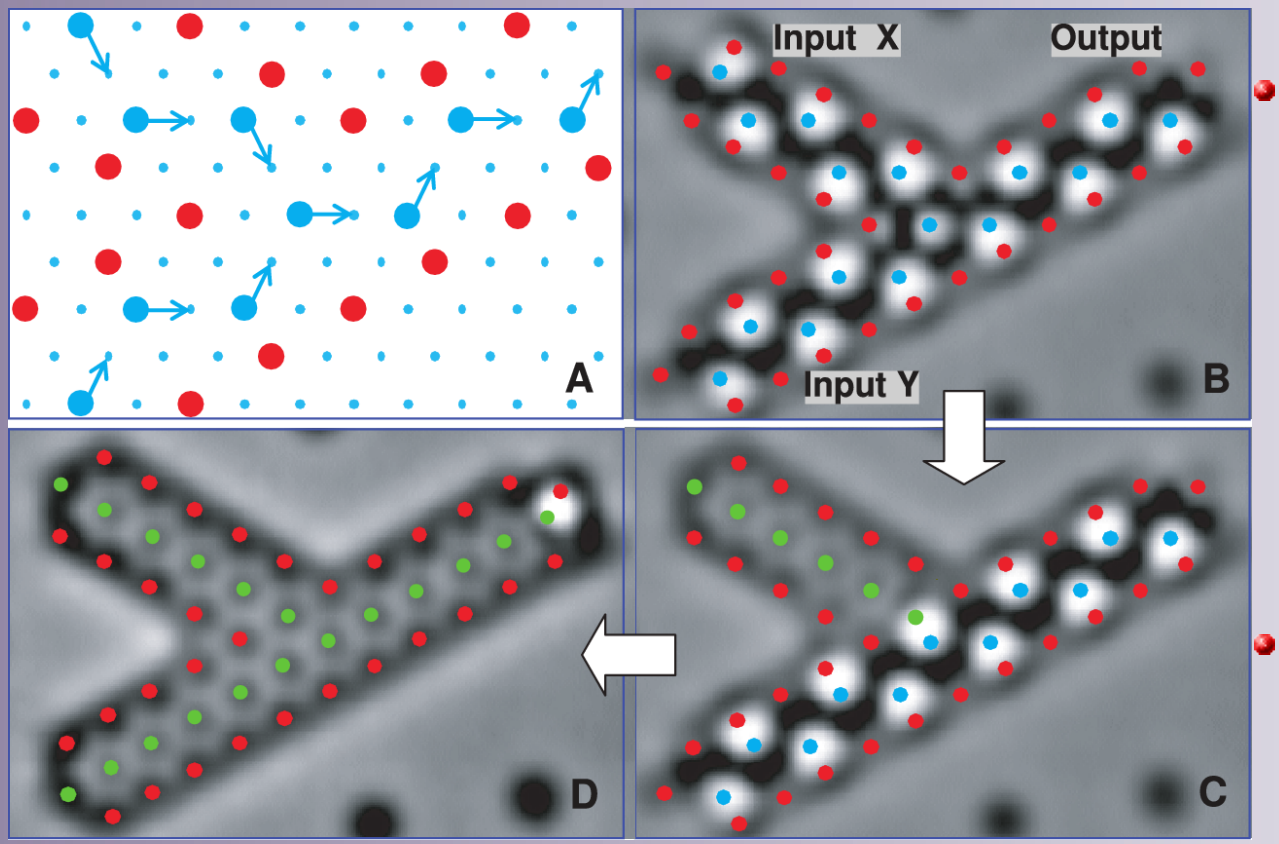
Cascades logic circuits

Logic AND Gate



- For setting up a chevron in the middle, both Input cascades have to be triggered
- STM Image 5.1nm by 3.4nm

● CO that hops ● after hopping

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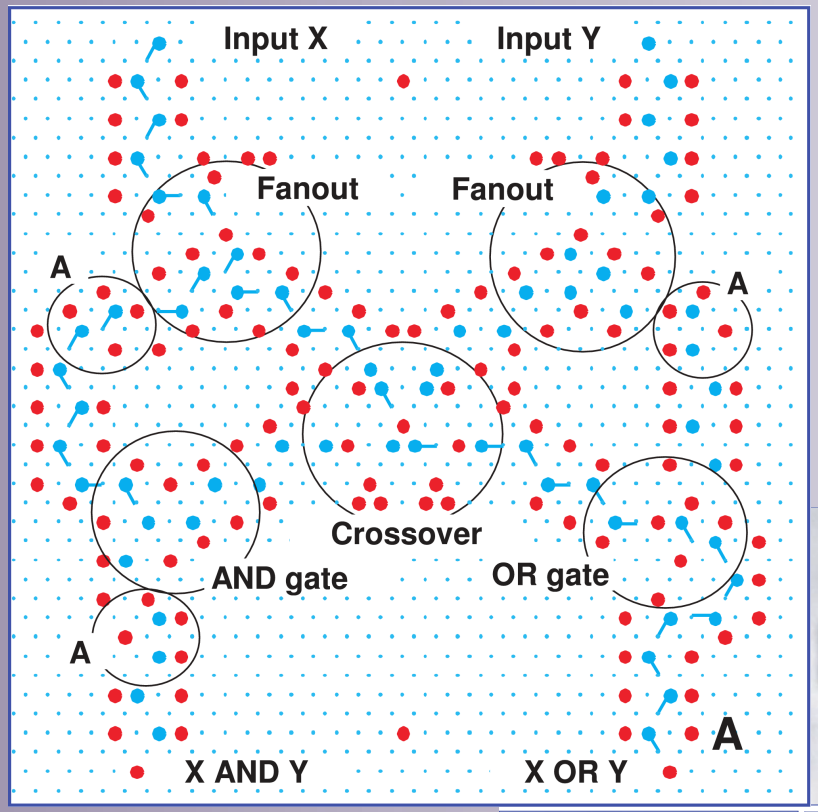
Cascades logic circuits

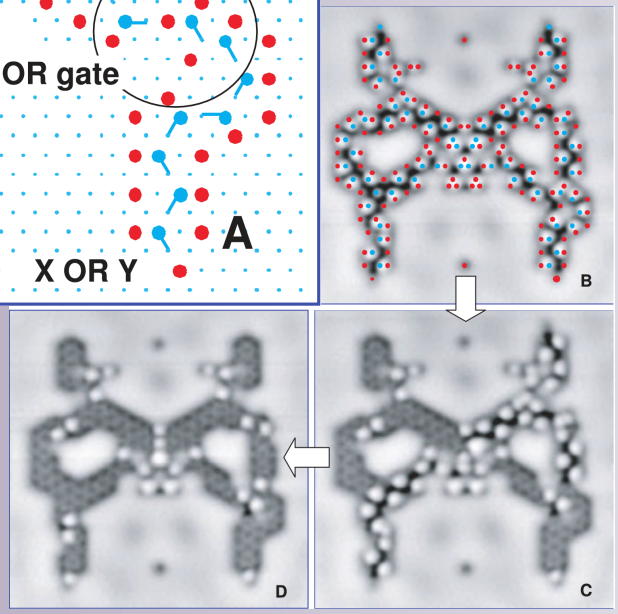
Two Input Sorter



computes logic AND and OR of the input

Fanout - duplicates the input signal

- alignment units labeled “A”



- Crossover – to pass the two signals through each other

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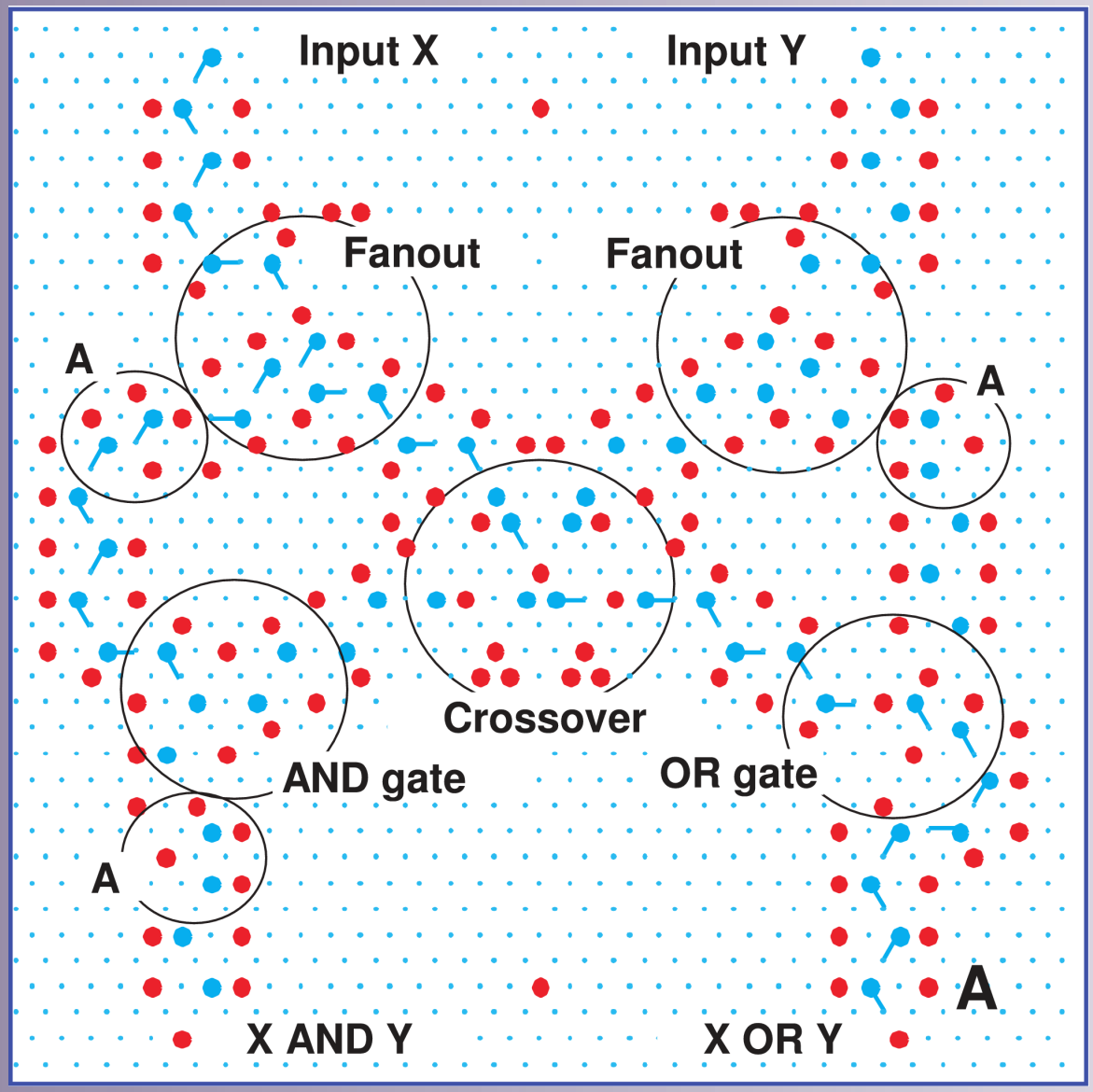
Cascades logic circuits



occasional backwards and premature hops observed in the Crossover, the Fanout and the OR Gate

(~1 per day)

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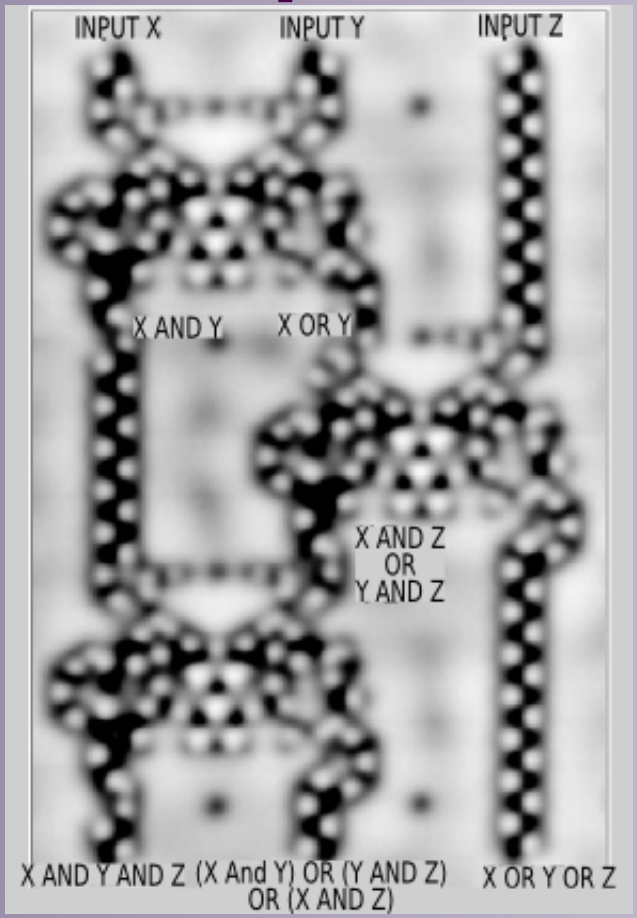
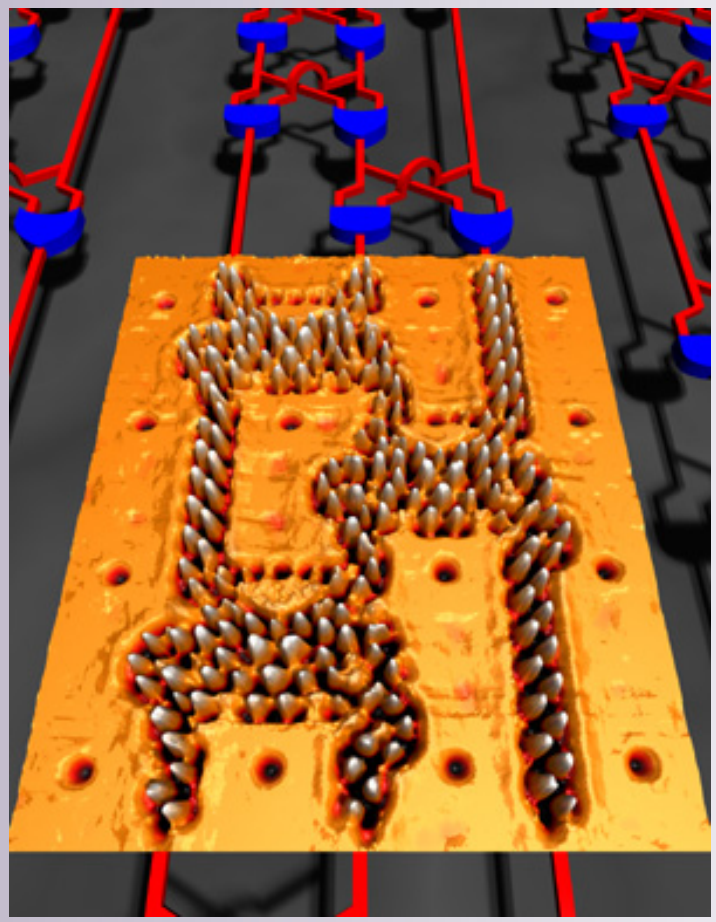
Cascades and Computing

Three-Input Sorter





STM Image
12nm x 17nm

propagation time at 5K:
~1 hour from Input to Output

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Conclusion

- Molecule cascades allow to study the motion of individual molecules.
- The direction and rate of molecular motion was engineered.
- Working digital-logic elements were built 260000 times smaller than conventional electronic devices.
- Only one-time calculations are possible → no reset mechanism.

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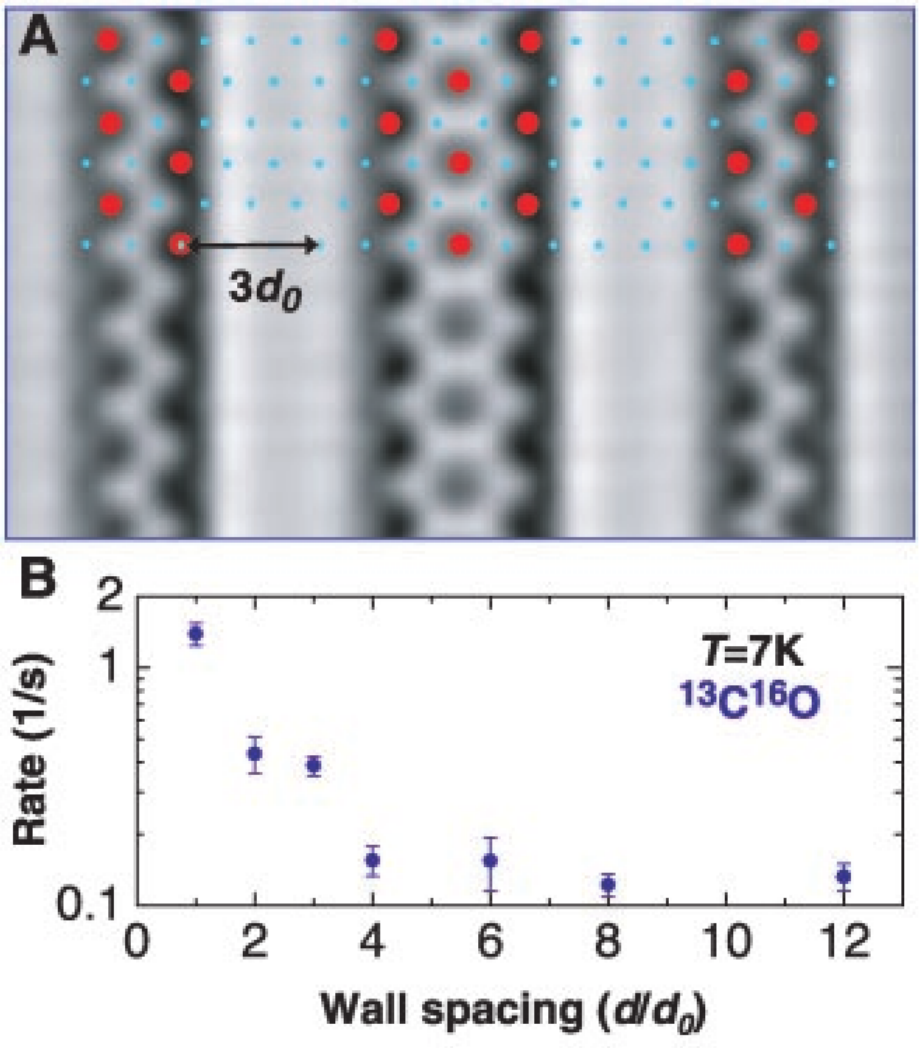
The hopping mechanism

Hopping rate vs. wall spacing



- Environmental influence on hopping rates:
  - nearby defects, steps
  - impurities
  - surface-state standing waves
  - and other CO molecules
- hopping rate is independent of wall spacing for d>4d0
  - enclosed cascades with CO walls
  - reduce environmental influences

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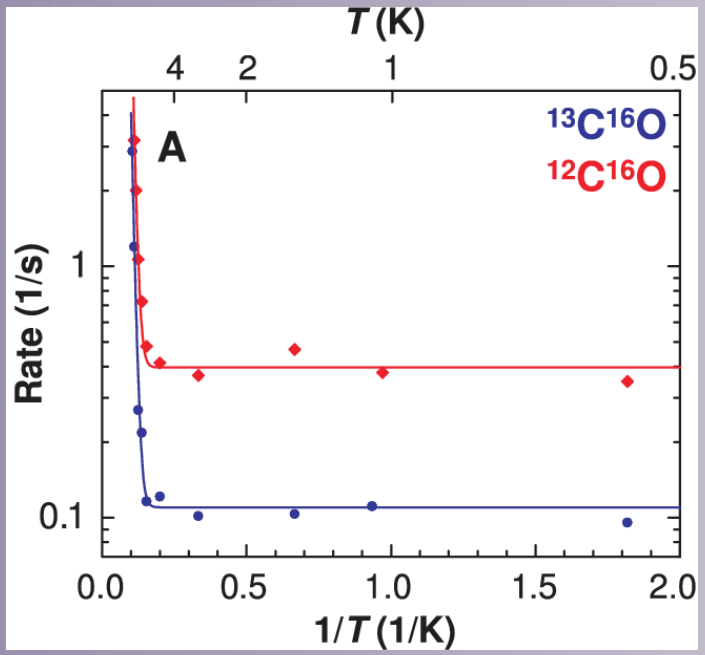
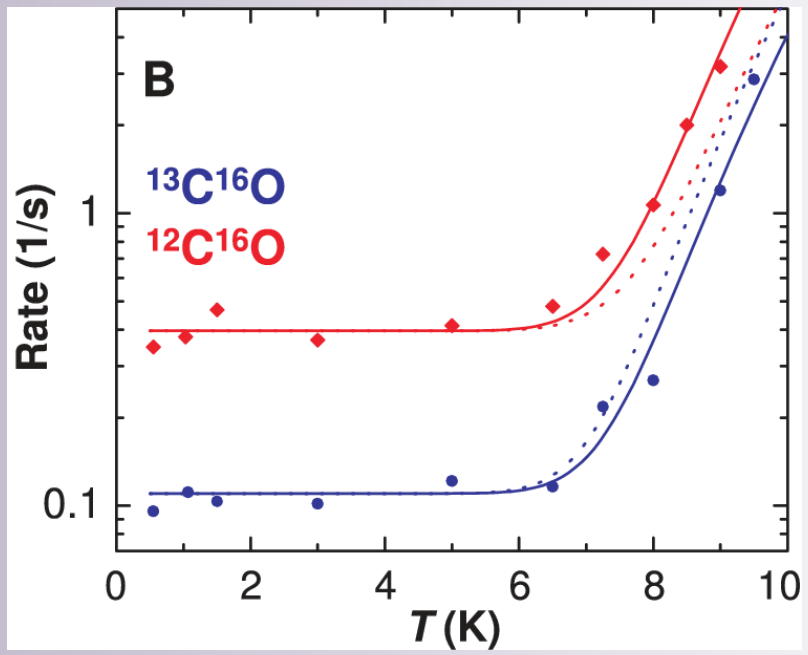
The hopping mechanism

Temperature dependency





- dotted line in B → fitted with same values for A and E
- thermally activated process dependent on the C isotope
- solid lines in A & B → with

$$E = (9.5 \pm 0.9)\,meV$$
$$A = 10^{(5.8\pm0.5)}\,s^{-1}\,for\,^{12}C$$
$$A = 10^{(5.4\pm0.5)}\,s^{-1}\,for\,^{13}C$$

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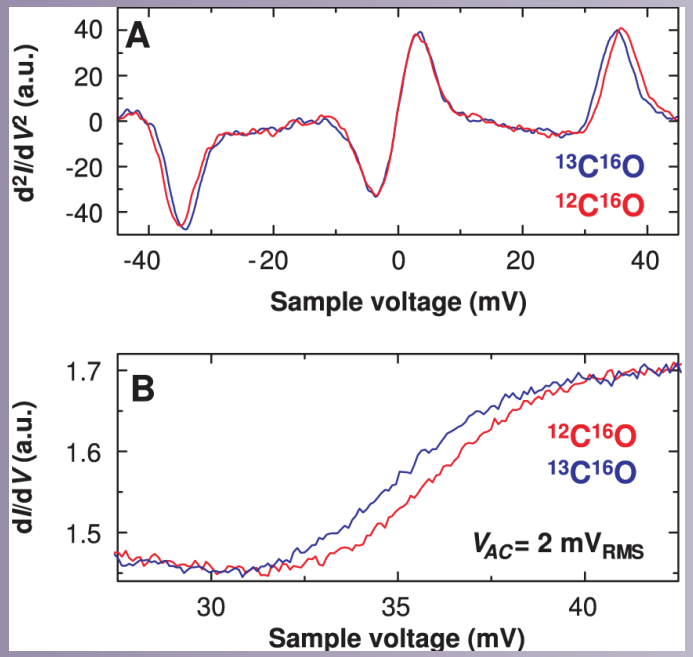
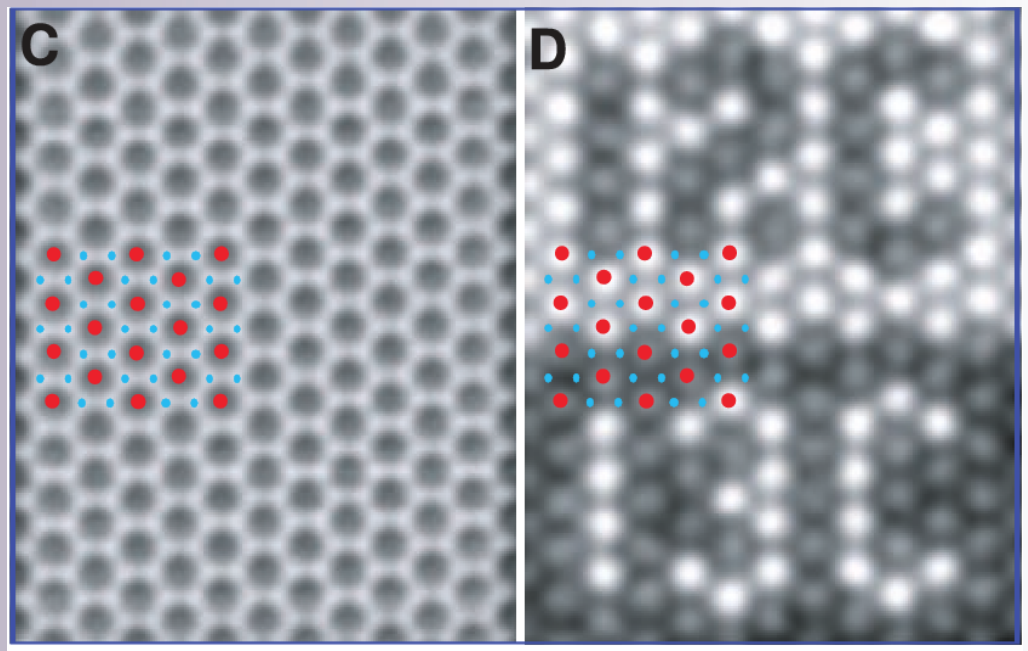
The hopping mechanism

Isotope dependency





- coabsorbed $^{12}C^{16}O$ and $^{13}C^{16}O$ by mixing isotope-selected gas in the room temperature vacuum chamber
- Picture done by IETS (Inelastic electron tunneling spectroscopy)

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The hopping mechanism

Model of the hopping rate

$$hopping\,rate[R] = \frac{(number\,of\,hops)}{(propagation\,time)}$$

$$R = R_{QT} + A \cdot e^{\left(\frac{-E}{Tk_B}\right)}$$

R ... hopping rate
R_{QT} ... tunneling rate
E ... activation energy
A ... Arrhenius Factor

- observed A (~10^5.5) is smaller than initial state vibrational frequencies (~10^12-10^13)
- in this case: tunneling from thermaly excited states of the molecule

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WKB Approximation

$$R_{QT} = A_T \cdot \exp\left[\frac{(-4 \cdot \pi^2 \cdot \sqrt{2m})}{h} \times \int_{initial}^{final} \sqrt{V_{(x)} - ZPE}\, dx\right]$$

m ... tunneling mass
V(x) ... potential
ZPE ... zero point energy
A_T ... attempt frequency

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