Spin-dependent tunneling through organic molecules: spin scattering by organic radicals

P. LeClair
Physics & Astronomy, MINT, University of Alabama

G.J. Szulczewski, A. Gupta, S. Street
Weihao Xu
Chemistry, MINT, University of Alabama

Dina Genkina, Abel Demisse
REU interns
Organic Spintronics

- Tunneling processes more crucial as length scales decrease
- Control with multiple degrees of freedom
- Spin transport & more general applications
- enable organic-based spintronics

- Organic materials are unique:
  - properties tailored through synthesis

- Fundamental understanding of transport
  - one molecular building block at a time
  - multiple degrees of freedom
  - interplay with optoelectronics?

- Create toolkit for device design
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Organic semiconductors
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\[ \text{Alq}_3 \]
Organic semiconductors

\[
\text{Alq}_3
\]

\[
\text{H}_2\text{TPP}
\]
Organic semiconductors

Alq₃

H₂TPP

Pc
Sample Preparation

La_{0.67}Sr_{0.33}MnO_3 film (50-100 nm) → SrTiO_3
Sample Preparation

$\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film (50-100 nm) $\rightarrow$ SrTiO$_3$ $\downarrow$ Pattern
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La$_{0.67}$Sr$_{0.33}$MnO$_3$ film (50-100 nm) → SrTiO$_3$ → Pattern → Clean with ~0.1% Br$_2$ in ethanol for 30 sec
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La$_{0.67}$Sr$_{0.33}$MnO$_3$ film (50-100 nm) → SrTiO$_3$ → Pattern → Vapor deposit organic

Clean with ~0.1% Br$_2$ in ethanol for 30 sec
Sample Preparation

La$_{0.67}$Sr$_{0.33}$MnO$_3$ film (50-100 nm)

SrTiO$_3$

Pattern

Vapor deposit organic

Vapor deposit Co and Al through shadow mask

Clean with $\sim$0.1% Br$_2$ in ethanol for 30 sec
Sample Preparation

La$_{0.67}$Sr$_{0.33}$MnO$_3$ film (50-100 nm)

SrTiO$_3$

↓ Pattern

↓ Vapor deposit organic

“Cross-bar” Area = 0.10 mm$^2$

↓ Vapor deposit Co and Al through shadow mask

Clean with ~0.1% Br$_2$ in ethanol for 30 sec
Current-voltage and conductance curves


Superconducting electrodes confirms tunneling

Co

15nm TPP

LSMO

Simmons fit:

\[ d = 2.32 \text{ nm} \]

\[ \phi = 0.72 \text{ eV} \]

0.5 K

11 K
Normalized MR versus LSMO surface polarization

Park et al. PRL 81, 1953 (1998)

no apparent spin loss through TPP

T dependence just LSMO
Meservey-Tedrow tunneling

• thin film SC in H (~2-3T)
  Zeeman split quasiparticle DOS
  measure $dI/dV \sim N_{sc}N_{fm}$

• nonmagnetic:
  symmetric -- equal # of spins

• magnetic:
  asymmetry = spin polarization

robust, microscopic theory

“directly” gives spin imbalance of tunneling current
T = 0.36 K
H = 3 T
H = 0 T
T = 500mK
P ~ 37%
H = 0
H = 3T
Al / AlOx / TPP / Co
polarization is not decreased by TPP
increased conductance at low bias, low T ...

evidence of magnetic excitations!

Magnetoresistance of Co/20 nm TPP/LSMO


sizable MR observed up to 40% at 10K
so what’s the problem?

• still to complicated

• need a simpler starting point for structure-property correlation

• so we go ‘back to the future’ … (again)
Molecular Tunnel Junctions

- *One layer* of a simple, flexible molecule - benzoic acid derivatives
- **Model system** for more complex molecules - ‘scaffolding’
- Correlate *transport* and *molecular structure*

**Structure**
- Photoemission (UPS,XPS)
- Raman/IR
- Inelastic electron tunneling

**Transport**
- Conductance (V,H,T)
- Spin-polarized tunneling
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![Molecule Diagram](image)
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Self-assembly yields well-ordered monolayers
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Al (~10 nm) → shadow mask
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↓ deposit benzoic acid from solution
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Al (~10 nm) → shadow mask

↓ deposit benzoic acid from solution

↓ Vapor deposit Co or Pb through shadow mask
Sample Preparation

1. Deposit Al (~10 nm)

2. Deposit benzoic acid from solution through a shadow mask.

3. "Cross-bar" with Area = 0.10 mm²

4. Vapor deposit Co or Pb through the shadow mask.
IETS: is there transport through the molecule?

- tunneling electrons excite vibrational modes
  - see Raman & IR modes
  - no strong selection rules

- when $eV \geq h\nu$
  - stepped increase in $dI/dV$
  - new set of final states available
  - unambiguous - transport through molecule

- example: studying model catalysts
  - CO on Rh/$\text{Al}_2\text{O}_3$ -- CO vibrations

“tunneling energy loss spectroscopy”

detail:
  - tiny signals … challenging
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How to measure a derivative?

\[ I(V_{dc} + \delta V_{ac} \cos \omega t) = I(V_{dc}) + \frac{dI}{dV}(\delta V_{ac} \cos \omega t) + \frac{d^2I}{dV^2} \left( \frac{\delta I_{ac}^2}{4} \cos(2\omega t) \right) + \ldots \]

- drive system with \( V_{dc} + \delta V_{ac} \sin \omega t \)
- measure response at \( \omega \)

**frequency / phase sensitive technique**

... lock-in amplifiers
(talk to Dr. Enders)
(1) original nice idea ...
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(2) the “Danny filter” ...

(3) implementation ...
$\frac{dl}{dV}$: lock in to $f$

$d^2l/dV^2$ (IETS): lock in to $2f$

‘constant resolution’ mode

software feedback to maintain modulation
Transport facilities

Quantum Design PPMS
\[ R(T,H) \]
\[ T: \text{350mK -- 400K} \]
\[ ^3\text{He fridge} \]
\[ H: \text{0 -- 7T} \]
scriptable …

+ 

Home-built electronics
\[ \frac{dI}{dV}(V,T) \]
\[ \frac{d^2I}{dV^2}(V,T) \]
IETS: we really have transport through the molecule
IETS: we really have transport through the molecule
ATR-FTIR

what is the state of the molecule?

is it still there?

JASCO FT/IR-4100_ATR
Scan #: 128
Resolution: 2 cm$^{-1}$
$T = 2K$

$\nu$: stretch; $\beta$: in-plane bend; $\gamma$: out-of-plane bend.

The University of Alabama
Co reacts with heavier halogens

Pb does not

halogen substitution leads to organic radicals
Conductance Through Benzoic Acids

- Vary para-substituent
- Controlled introduction of radicals

![Graph showing conductance through benzoic acids](image)

The University of Alabama
Center for Materials for Information Technology
A NSF Materials Research Science and Engineering Center
size of zero-bias anomaly scales with degree of reaction
only very tiny effects for fluorobenzoic acid (or cyano)
slightly larger for chlorobenzoic acid
huge for iodobenzoic acid
when we have a reaction …

… there is an unpaired electron

… which means an unpaired spin

… which gives a Kondo resonance

\( (T_k \sim 20K) \)

(wacky quantum interference)

(many body effect)
Al/Al\textsubscript{2}O\textsubscript{3}/ 4-iodobenzoic acid / Co \hspace{1cm} T = 2K

\begin{itemize}
  \item H=0
  \item H=7T
\end{itemize}

in a field, Kondo peak suppressed small “well” carved out of it...
Spin-dependent Scattering by Organic Radicals

- Organic radicals = unpaired electron
- Should have ‘normal’ spin flip scattering
- Revealed through application of H

fit gives $g \sim 2 \ldots$ consistent
More details:

- fit to high field data gives $g \sim 2$ … expected
- signature logarithmic $(V,T)$ dependence of Kondo peak in $H=0$
- Kondo, $H$-dependent part are \textit{small terms} \\
V-independent parts \textit{much} larger \\
spin scattering \textit{dominates} conductance
Building a Molecular Spin Transport Toolkit

• Porphyrin derivatives (E. Galoppini, Rutgers)
  - control orientation
  - Dr. Choe ...

• Phthalocyanine derivatives
  - CoPc, F$_{16}$CuPc
  - tune spin-orbit scattering via $\text{TM}$ ion

• Lanthanide complexes
  - $\text{RE}^{3+}$ controls spin dynamics
  - strong exchange
Building a Molecular Spin Transport Toolkit

• new families of (known) molecules
  spin transport is *unknown*

• build knowledge block by block

• systematic variation

• new tools and synergy
  transport $\leftrightarrow$ structure

• *designer toolkit for spin transport*

• Spin-dependent scattering *dominates with radicals*
  - General mechanism!

thanks to: NSF MRSEC grant No. DMR 0213985.
\[ G = G^{(1)} + G^{(2)} + G^{(3)} \]
$G^{(1)}$

$G^{(2)}$

$G^{(3)}$

$G = G^{(1)} + G^{(2)} + G^{(3)}$
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• Understand spin injection & transport
• Enable organic-based spintronics

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Two terminal: OLED, MTJ, spin valve
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Three terminal: FET, logic, memory
Two terminal: OLED, MTJ, spin valve