

第三章 尺寸

3.1 介观体系

3.2 纳米体系

3.3 原子团簇

3.1 介观体系

1. 电子波的干涉 金属的电导率

$$\sigma_0 = \frac{ne^2\tau}{m^*}$$

m^* : 载流子(电子)的有效质量 n : 电子浓度

τ : 输运驰豫时间 $\rightarrow$ 处于某动量本征态的电子的平均寿命

在二维情况下: $n = \frac{k_F^2}{2\pi}$ k_F 为费米波矢

$$l = v_F \tau = m^* v_F \frac{\tau}{m^*} = \hbar k_F \frac{\tau}{m^*} \quad \text{电子输运平均自由程}$$

$$\sigma_0 = \frac{k_F^2}{2\pi} \cdot \frac{e^2}{\hbar k_F} \cdot l = \frac{e^2}{2\pi^2 \hbar} \cdot \pi k_F l = \sigma_{00} \pi k_F l \quad \sigma_{00}: \text{电导量子}$$

输运弛豫时间包含了各种相互作用的贡献：

电子—杂质，电子—声子，电子—电子

$$\frac{1}{\tau} = \frac{1}{\tau_{e-imp}} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{e-e}} + \dots = \frac{1}{\tau_0} + \frac{1}{\tau_\varphi}$$

{ 电子与静态散射中心的 散射：弹性散射

{ 电子与动态散射中心的 散射：非弹性散射

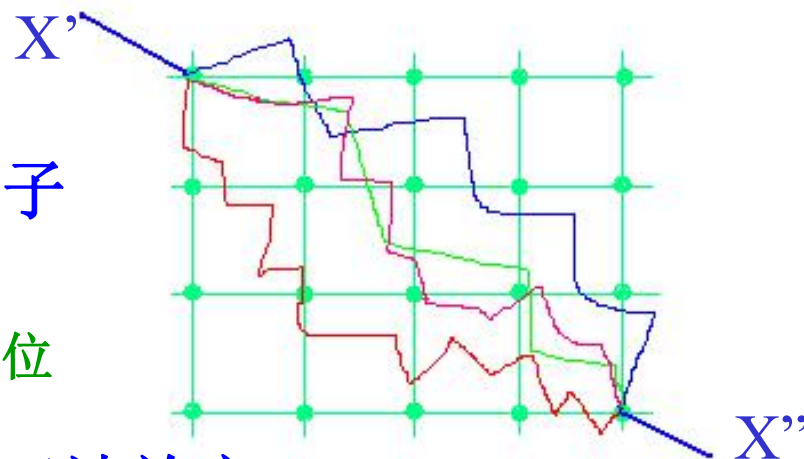
较纯金属：杂质散射贡献较小，电子—电子相互作用由于传导电子的屏蔽效应而变得很弱。在温度较高时，声子散射起主要作用，它决定了电导率随温度变化的规律。随温度的降低，声子浓度不断减少，而杂质的数量不变，因此电导将趋于常数(剩余电阻)。

电子被看作粒子，各种相互作用都被纳入相应的弛豫时间，电子作为波的运动特征—相位被完全忽略了。

简化的合理性：

电子沿不同的布朗运动路径从 X' 点到达 X'' 点(假设所以路径上电子经历的散射为弹性)：

分波： $A_n = |A_n| \exp(i\varphi_n)$ φ_n 为其相位



$$|\sum_n A_n|^2 = \sum_n A_n^2 + \sum_{n \neq m} A_n A_m^* \quad \text{干涉效应}$$

$\cos(\varphi_n - \varphi_m)$ 路径无规，平均 $\overline{\cos(\varphi_n - \varphi_m)} = 0$

某些特殊条件下，干涉效应不为零：

- 沿一闭合路径反向运动的两电子分波，具有时间反演对称性。两电子分波的叠加在总平均中不抵消
- 电子散射的可能路径不是无限多，而是局限于若干个有限路径时

(a). 弱局域化电导修正

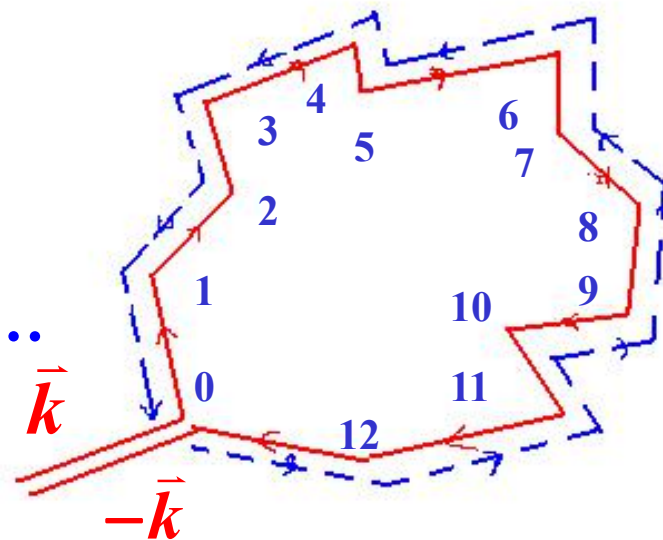
闭合路径：电子在固体中扩散运动时以一定的概率返回它的出发点，这种路径称之为闭合路径。

$\vec{k}$ 态的电子从0点开始：0→1→2→3...
→12→0 $-\vec{k}$, 波函数为 A_+

等概率地：

$\vec{k}$ 态的电子从0点开始：0→12→11→10...
→1→0 $-\vec{k}$, 波函数为 A_-

$$|A_+| = |A_-| = A$$



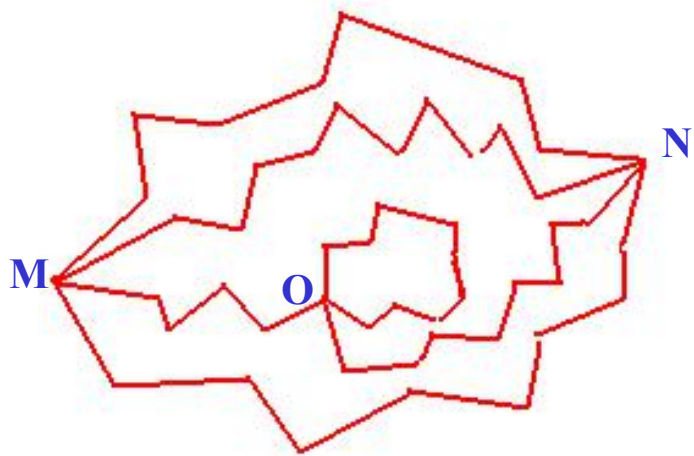
这两个路径的顺序具有时间反演对称性，称之为时间反演路径 (time reversal path)

对所有散射为弹性散射的情形，可证明，电子受相同的杂质散射从 $\vec{k}'$ 态到 $\vec{k}''$ 态和从 $-\vec{k}''$ 态到 $-\vec{k}'$ 态所附加的相移 $\delta\varphi$ 是相同

A_+ 与 A_- 具有相同的振幅，相同的相位：

$$|A_+ + A_-|^2 = |A_+|^2 + |A_-|^2 + 2 \operatorname{Re} A_+ A_-^* = 4A^2$$

虽然巨大数量的电子扩散路径的电子分波的干涉趋向于相互抵消，但经过时间反演路径的电子波的干涉却相互增强。电子回到途中某一点几率的增加，意味着观察点N发现电子的几率下降，导致电导率的减小或电阻率的增加，呈现对经典电导率的量子力学改正——弱定域化的物理图象，是量子力学波函数叠加原理导致宏观可观察后果的独特范例。



计及量子效应之后，电子似乎更趋向于呆在原点

弱定域化引起的电导变化：

假定处于 $\vec{k}$ 态的电子可能被散射到费米面上的Z个状态
该电子被散射到 $-\vec{k}$ 的几率为1/Z，而与经历的中间态散射
次数n无关。

电子处于动量本征态 $\vec{k}$ 的平均寿命 τ_0
费米波矢的不确定量为： π / l $l = v_F \tau_0$ 自由程

二维：不确定量构成的圆环面积： $2\pi k_F \cdot \frac{\pi}{l} = \frac{2\pi^2 k_F}{l}$

K空间的态密度为： $(2\pi)^{-2}$

圆环所包含的状态数： $Z = \frac{k_F}{2l}$

$\vec{k} \rightarrow -\vec{k}, \vec{k} \rightarrow -\vec{k} + \vec{q}$ 都对相关散射有贡献

初态+末态的动量 $\rightarrow \vec{q}$ 能量差为： $\Delta E = \hbar \vec{q} \cdot \vec{v}_F$

在一次散射时间间隔 τ_0 内产生的相移： $\Delta E \tau_0 / \hbar = \vec{q} \cdot \vec{v}_F \cdot \tau_0$

中间态上的相移不同，位相平方相加，叠加n次散射后：

$$(\Delta\varphi)^2 = n \overline{(\bar{q} \cdot \bar{v}_F \tau_0)^2} = n \frac{(qv_F \tau_0)^2}{2} = Dq^2 t, \quad D = v_F^2 \tau_0 / 2 : \text{二维扩散系数}$$

$t = n\tau_0$ 为电子从 $\bar{k}$ 态被散射到 $-\bar{k}$ 态的时间

$(\bar{q} \cdot \bar{v}_F)^2$ 的平均值为 $(qv_F)^2 / 2$ (二维) $(qv_F)^2 / 3$ (三维)

电子回波产生的反向粒子流：

$$I_{-k} = \frac{1}{(2\pi)^2} \int dq^2 Z^{-1} \exp(-Dq^2 t) = \frac{\tau_0}{\pi k_F l t}, \quad I_{-k} \sim \frac{1}{t}$$

若一个电子在 $t=0$ 时处于 k 态，根据弛豫时间近似，其动量 $\bar{k}$ 以特征时间 τ_0 指数衰减，而由于干涉回波产生的反向动量 $-\bar{k}$ 则随时间的倒数衰减，且在 $t = \tau_\varphi$ 时消失，那么这个电子对于平均动量的贡献为：

$$\bar{k} \left[\int_0^\infty e^{-t/\tau_0} dt - \int_{\tau_0}^{\tau_\varphi} \frac{\tau_0}{\pi k_F l t} dt \right] = \bar{k} \tau_0 \left[1 - \frac{1}{\pi k_F l} \ln \frac{\tau_\varphi}{\tau_0} \right]$$

电导也将以括号内的因子减少：

$$\sigma = \frac{ne^2\tau_0}{m^*} \left[1 - \frac{1}{\pi k_F l} \ln \frac{\tau_\phi}{\tau_0} \right] = \sigma_0 - \sigma_{00} \ln \frac{\tau_\phi}{\tau_0} = \sigma_0 - \Delta\sigma$$

$\Delta\sigma$ 为弱局域化电导修正

$\Delta\sigma$ 为 σ_{00} 量级, $10^{-6} \sim 10^{-5} \text{S}$ 低温下，一般金属薄膜的电导率 $0.01 \sim 0.1 \text{S}$ 。

$\Delta\sigma \propto \ln \frac{\tau_\phi}{\tau_0}$ 在电子平均自由程较小的样品中容易观察到这种现象：淬火薄膜或掺氧薄膜

$\Delta\sigma$ 对温度的依赖取决于 $\ln \tau_\phi$. 如相位驰豫主要来源于 $e-e$: $\tau_\phi \propto T^{-p}$

$\Delta\sigma \propto -p \ln T \rightarrow \Delta R \propto p \ln T$ 低温下的电阻对数上升 现象

(b). 正常金属中的Aharonov-Bohm (AB) 效应

经典电磁学：

$\vec{E}, \vec{B}$ 麦克斯韦方程，标量势 $\varphi(\vec{r})$, 矢量势 $\vec{A}(\vec{r})$

$$\vec{E} = -\nabla \varphi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \vec{B} = \nabla \times \vec{A}; \text{当 } \varphi, \vec{A} \text{ 作规范变换:}$$

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla \chi(\vec{r}, t), \varphi \rightarrow \varphi' = \varphi - \frac{1}{c} \frac{\partial}{\partial t} \chi(\vec{r}, t)$$

$\vec{E}$ 和 $\vec{B}$ 都不改变。 χ 任意 $\rightarrow$ 物理观测量与之无关 $\rightarrow$ 规范不变性

量子力学：

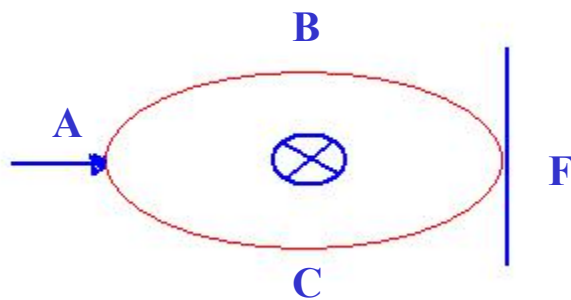
电磁场中运动的粒子方程

$$i\hbar \frac{\partial \psi}{\partial t} = \left[\frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right)^2 + q\varphi \right] \psi, \quad \left. \begin{matrix} \vec{A} \\ \varphi \end{matrix} \right\} \text{物理上的实在}$$

$$i\hbar \frac{\partial \psi}{\partial t} = [\frac{1}{2m} (\vec{p} - \frac{q\vec{A}}{c})^2 + q\phi] \psi$$

规范变换 $\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla \chi(\vec{r}, t), \phi \rightarrow \phi' = \phi - \frac{1}{c} \frac{\partial}{\partial t} \chi(\vec{r}, t)$

$$\psi \rightarrow \psi' = \psi e^{iq\chi/\hbar c}$$



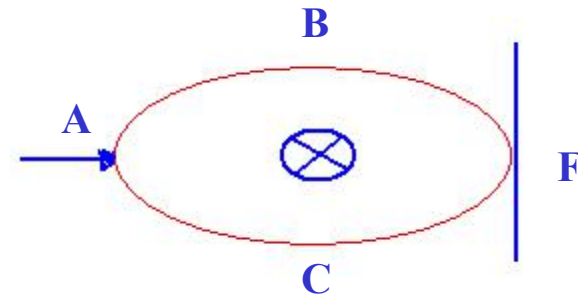
经典物理：电子束通路上没有磁场，没有磁力作用在电子上，螺线管中磁场不会产生任何影响。

量子力学：电子将感受到与磁通量相联系的矢势存在，波函数将附加一与矢势A有关，依赖于路径的相位。

$$ABF : \psi_1 = \psi_1^0 e^{ie/\hbar c \int_1 \vec{A} d\vec{l}} = \psi_1^0 e^{i2\pi/\Phi_0 \int_1 \vec{A} d\vec{l}}, \quad \Phi_0 = \frac{hc}{e} \quad \text{量子磁通}$$

$$ACF : \psi_2 = \psi_2^0 e^{i2\pi/\Phi_0 \int_2 \vec{A} d\vec{l}}$$

$$F \text{ 点干涉 } \psi = \psi_1 + \psi_2$$



$$\rightarrow |\psi|^2 = |\psi_1^0|^2 + |\psi_2^0|^2 + 2\psi_1^0 \psi_2^0 \cos\left[\frac{2\pi}{\Phi_0} \left(\int_1 \vec{A} d\vec{l} - \int_2 \vec{A} d\vec{l}\right)\right]$$

$$\text{若 } \psi_1^0 = \psi_2^0 = \psi_0$$

$$\rightarrow |\psi|^2 = 2|\psi_0|^2 + 2|\psi_0|^2 \cos \frac{2\pi\Phi}{\Phi_0}, \Phi = \oint \vec{A} \cdot d\vec{l}$$

干涉强度依赖于两条路径封闭的磁通总量 Φ ，并以周期 Φ_0 振荡。

观察AB效应：

电子束不受散射，相位相干不受破坏：高真空或超导体
正常金属扩散区？电子经多次散射，走着无规行走路径—可观察

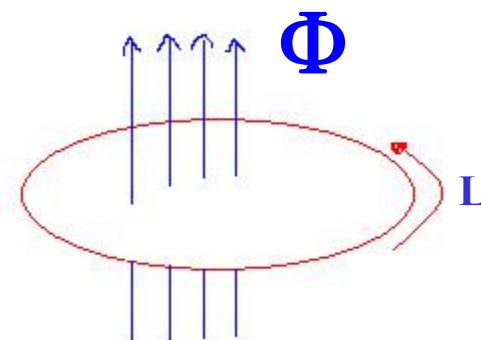
对一维理想金属环，如果有磁通 Φ 穿过中空区，这个环的所有物理性质随 Φ 以 Φ_0 为周期变化

$$H = \frac{1}{2m} (-i\hbar \nabla + \frac{e}{c} \vec{A})^2 \quad H\psi = E\psi$$

$$\begin{cases} \psi(L) = \psi(0) \\ \left. \frac{d\psi}{dx} \right|_{x=L} = \left. \frac{d\psi}{dx} \right|_{x=0} \end{cases} \quad x = r\theta, L = 2\pi r$$

作规范变换，矢势 $\vec{A}$ 与波函数 $\psi(x)$ 的变换为：

$$\vec{A} \rightarrow \vec{A}' = \vec{A} - \nabla \chi, \quad \psi \rightarrow \psi' = \psi e^{i\frac{e}{\hbar c} \chi}$$



选择 χ 使 $\bar{A}' = 0$:
$$\frac{-\hbar^2}{2m} \cdot \frac{d^2}{dx^2} \psi'(x) = E \psi'(x)$$

$$\begin{cases} \psi'(L) = \psi'(0)e^{i2\pi\phi/\phi_0} \\ \left. \frac{d\psi'}{dx} \right|_{x=L} = \left. \frac{d\psi'}{dx} \right|_{x=0} e^{i2\pi\phi/\phi_0} \end{cases} \text{其中 } \phi \text{ 为穿过环中心的磁通}$$

$$\phi_0 = \frac{hc}{e} : \text{磁通量子。}$$

当 $\phi \neq m\phi_0$ (m 为整数) 时，磁场存在使边界条件发生改变

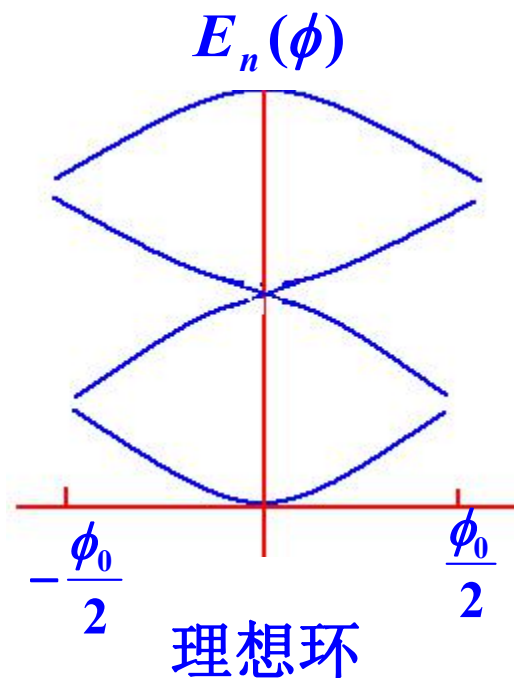
令方程的解: $\psi'(x) \sim e^{ikx} \rightarrow k_n = \frac{2\pi}{L} \left(n + \frac{\phi}{\phi_0} \right), n = 0, \pm 1, \pm 2, \dots$

能量本征值为:
$$E_n(\phi) = \frac{\hbar^2 k_n^2}{2m} = \frac{4\pi^2 \hbar^2}{2mL^2} \left(n + \frac{\phi}{\phi_0} \right)^2$$

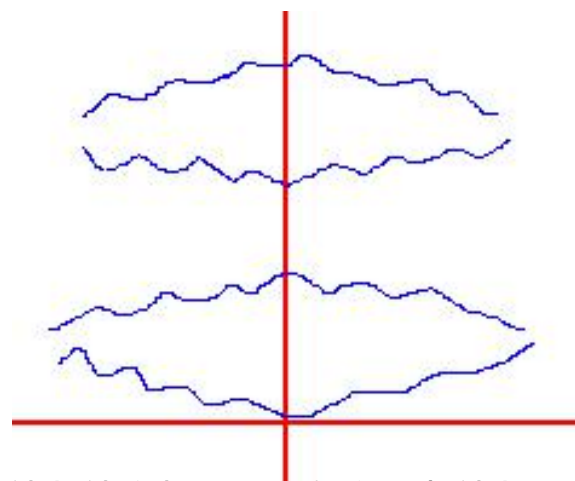
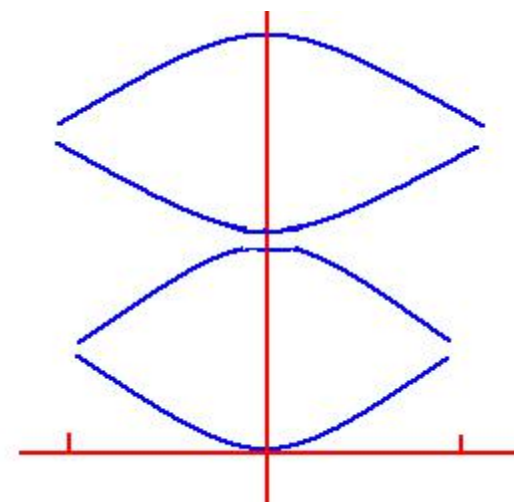
$E_n(\phi)$ 是 ϕ 的偶函数，以 ϕ_0 为周期。

上述问题与周期为 L 的一维能带问题相似：

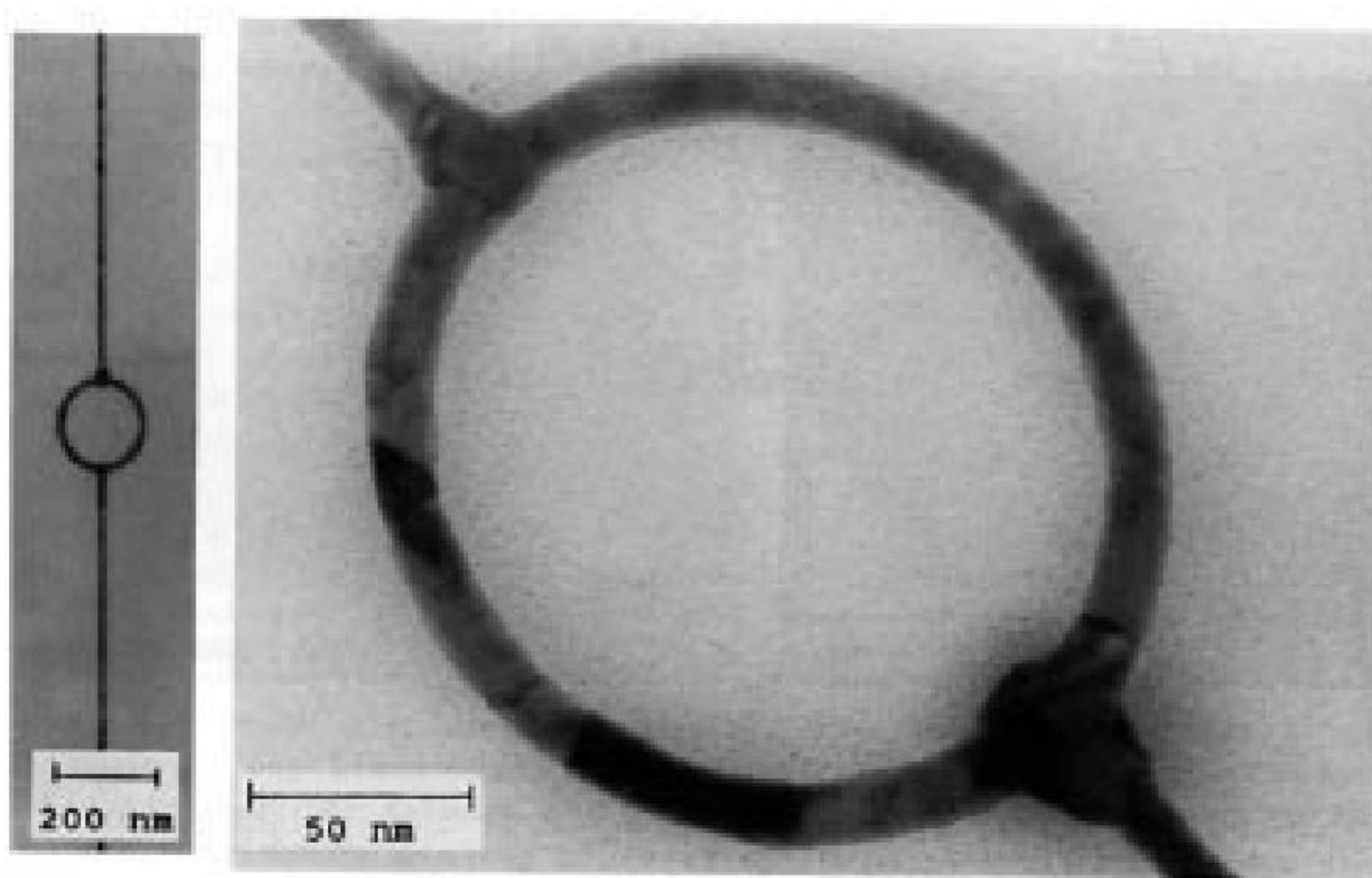
$$\frac{2\pi\phi}{\phi_0} \rightarrow kL \quad \text{一一对应}$$



杂质 $\rightarrow$ Peierls



非理想环



实验：1983年，Au的平均直径为245nm, 环宽30nm

AAS效应：除了观察到AB效应，还观察到周期为 $\frac{hc}{2e}$ 的效应
振幅只有AB效应的4%

缘由：弱局域化效应

矢势沿顺时针方向路径 提供相变改变 ϕ

矢势沿逆时针方向路径 提供相变改变 $-\phi$

相位差 $2\phi \rightarrow \frac{hc}{2e}$ 周期

2. 介观体系的电导

(1) Kubo (久保公式)

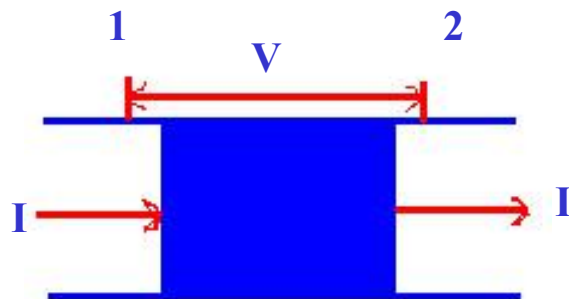
线性响应理论：非局域响应关联函数 $\vec{\sigma}(\vec{x}_1, \vec{x}_2)$

$$\hat{H}_0 \psi_\alpha = \varepsilon_\alpha \psi_\alpha, \hat{H}_0 : \text{自由电子体系无外电场}$$

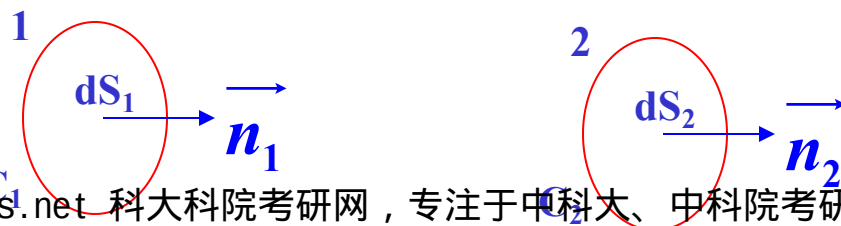
$$\vec{\sigma}(\vec{x}_1, \vec{x}_2) = \frac{e^2 \hbar^3 \pi}{4m^2} \int d\alpha \int d\beta f'(\varepsilon_\alpha) \delta(\varepsilon_\alpha - \varepsilon_\beta) \omega_{\beta\alpha}(\vec{x}_1) \omega_{\alpha\beta}(\vec{x}_2)$$

$$\omega_{\alpha\beta} \equiv \psi_\alpha^*(\vec{x}) \nabla \psi_\beta(\vec{x}) - \nabla \psi_\alpha^*(\vec{x}) \psi_\beta(\vec{x})$$

电导系数g:



$$g = - \int_{C_1} dS_1 \int_{C_2} dS_2 \vec{n}_1 \vec{\sigma}(\vec{x}_1, \vec{x}_2) \vec{n}_2$$



(2) Landauer公式：两电极视为理想导体，被测器件视为一势垒，器件的电导系数就一定依赖于电子波的穿透系数T：

$$g = \frac{e^2}{h} \frac{T}{1-T} \quad T \rightarrow 1, g \rightarrow \infty$$



(3) Landauer-Buttiker公式：

一根无穷长理想导线中独立电子的Shordinger方程：

$$H = \frac{1}{2m} \hat{P}^2 + V(x, y), \text{任一本征函数}$$

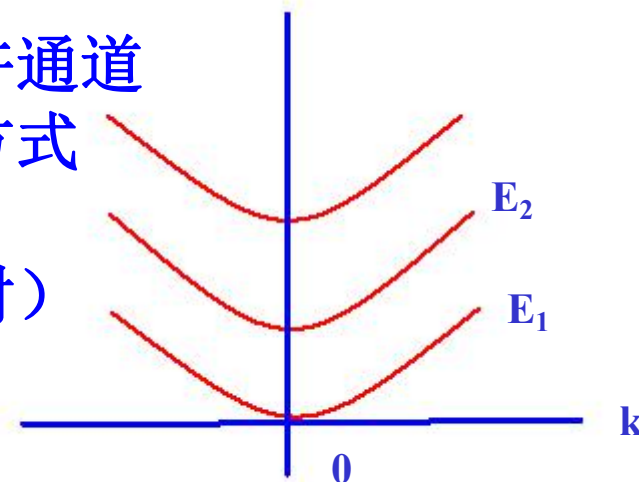


$$\psi_{\alpha k}(x, y, z) = \frac{1}{\sqrt{2\pi}} \exp(ikz) \phi_{\alpha k}(x, y), -\infty < k < \infty, \phi_{\alpha k}(x, y) \text{ 归一}$$

$$\text{本征值: } E_{\alpha k} = E_{\alpha} + \frac{\hbar^2 k^2}{2m}, \quad E_{\alpha} \text{ 由下列方程解出:}$$

$$\left[\frac{1}{2m} (\hat{P}_x^2 + \hat{P}_y^2) + V(x, y) \right] \phi_{\alpha k}(x, y) = E_{\alpha} \phi_{\alpha k}(x, y)$$

每条曲线代表一个横向子能带→容许通道
 在每个容许通道中电子将以行波的方式
 传播，从而引起电荷的流动。
 给定波矢量 $k>0$ ，电荷既可沿 $+k$ （入射）
 也可沿 $-k$ （反射）流动。



计算 $T=0K$ ，导线中第 α 个通道上的入射电流 I_α

μ ：导线中电子气的化学势， $V_{\alpha k}$ 为容许态 $\psi_{\alpha k}$ 中的电子群速度

$$V_{\alpha k} = \frac{1}{\hbar} \frac{\partial E_{\alpha k}}{\partial k}$$

$$\begin{aligned}
 I_\alpha &= \int_0^{K_{\max}} (eV_{\alpha k}) \frac{dk}{2\pi} = \int_{E_\alpha}^{\mu} (eV_{\alpha k}) \frac{dk}{dE_{\alpha k}} \frac{dE_{\alpha k}}{2\pi} = \int_{E_\alpha}^{\mu} (eV_{\alpha k}) \frac{1}{\hbar \left(\frac{1}{\hbar} \frac{dE_{\alpha k}}{dk} \right)} \frac{dE_{\alpha k}}{2\pi} \\
 &= \int_{E_\alpha}^{\mu} eV_{\alpha k} \frac{1}{\hbar V_{\alpha k}} \frac{dE_{\alpha k}}{2\pi} = \frac{e}{\hbar} (\mu - E_\alpha)
 \end{aligned}$$

被测器件视为一块不均匀散射媒质，它将理想导线1中入射而来的一束渐近行波散射到导线2中的某些容许通道(透射波)及导线1中的某些容许通道(反射波)中。

a. 计算两端单通道器件电导系数的Landauer-Buttiker公式
导线宽度很窄，各子能带之间的能差很大，最低子能带可被电子占据，成为唯一的容许通道。

1, 2导线由相同导线组成：

$$E_{\alpha 1} = E_{\alpha 2} = E_0$$

令 T_{ij} 为导线 i 到导线 j 的电子穿透几率 : $T_{12} = T_{21} = T$

$$\text{从 } 1 \rightarrow 2, \quad I_1 = T I_{1\alpha} = T \frac{e}{h} (\mu_1 - E_0)$$

$$\text{从 } 2 \rightarrow 1, \quad I_2 = T I_{2\alpha} = T \frac{e}{h} (\mu_2 - E_0)$$

$$1 \rightarrow 2 \text{ 净电流: } I = I_1 - I_2 = T \frac{e}{h} (\mu_1 - \mu_2) = T \frac{e^2}{h} (V_1 - V_2)$$

$$g_c = \frac{I}{V_1 - V_2} = \frac{e^2}{h} T \quad \text{Buttiker公式}$$

$$g = \frac{e^2}{h} \frac{T}{1-T} \quad g_c = \frac{e^2}{h} T \quad \rightarrow \quad g_c^{-1} = g^{-1} + \frac{h}{e^2}$$

g^{-1} : 由电子的自洽屏蔽引起 的势垒电阻

$\frac{h}{e^2}$: 两端的接触电阻

总电阻 g_c^{-1} 是势垒电阻及两个接触 电阻之和 $\rightarrow$ 实际测量电阻值

b. 计算两端多通道器件电导系数的Landauer-Buttiker公式
导线有限宽度，电子将填充其数个子能带(N)

给定能量 ε ，令 $T_{ij}(\varepsilon) = |t_{ij}(\varepsilon)|^2$ ， $R_{ij}(\varepsilon) = |r_{ij}(\varepsilon)|^2$

T_{ij} : 从左边第 j 个通道穿透到右边第 i 个通道的几率

R_{ij} : 从左边第 j 个通道反射到左边第 i 个通道的几率

总的透射进入第 i 个通道的几率 (右): $T_i(\varepsilon) = \sum_j T_{ij}(\varepsilon)$

总的反射进入第 i 个通道的几率 (左): $R_i(\varepsilon) = \sum_j R_{ij}(\varepsilon)$

定义另一套: $T_i'(\varepsilon) = \sum_j T_{ij}'(\varepsilon)$ (左) $R_i'(\varepsilon) = \sum_j R_{ij}'(\varepsilon)$ (右)

电子是独立的，精细平衡条件:

$$R_i'(\varepsilon) + T_i(\varepsilon) = 1 \quad R_i(\varepsilon) + T_i'(\varepsilon) = 1$$

改写两端单通道器件的净电流表达式:

$$I = T(E_F) \frac{e}{h} (\mu_1 - \mu_2) = \frac{e}{h} \int_0^\infty dE [T_1(E) f_1(E) - T_2(E) f_2(E)]$$

多通道:

$$I = \frac{e}{h} \int_0^\infty dE \left[f_1(E) \sum_i T_i(E) - f_2(E) \sum_i T_i'(E) \right]$$

$$T_i(E) = T_i'(E)$$

$$\text{上式} = \frac{e}{h} \int_0^\infty dE [f_1(E) - f_2(E)] \sum_i T_i(E)$$

当 $\mu_1 - \mu_2$ 很小时

$$\sum_i T_i(\mu_1) \approx \sum_i T_i(\mu_2) \approx \sum_i T_i(E_F)$$

$$I \approx \frac{e}{h} \sum_i T_i(E_F) \int_0^\infty dE [f_1(E) - f_2(E)]$$

$$= \frac{e}{h} \sum_i T_i(E_F) (\mu_1 - \mu_2) = \frac{e^2}{h} \sum_i T_i(E_F) (V_1 - V_2)$$

$$g_c = \frac{I}{V_1 - V_2} = \frac{e^2}{h} \sum_i \sum_j |t_{ij}(E_F)|^2 = \frac{e^2}{h} \text{Tr}(t^+ t)$$

$t \equiv (t_{ij}(E_F))$ 为穿透系数矩阵

3. 普适电导涨落 (UCF)

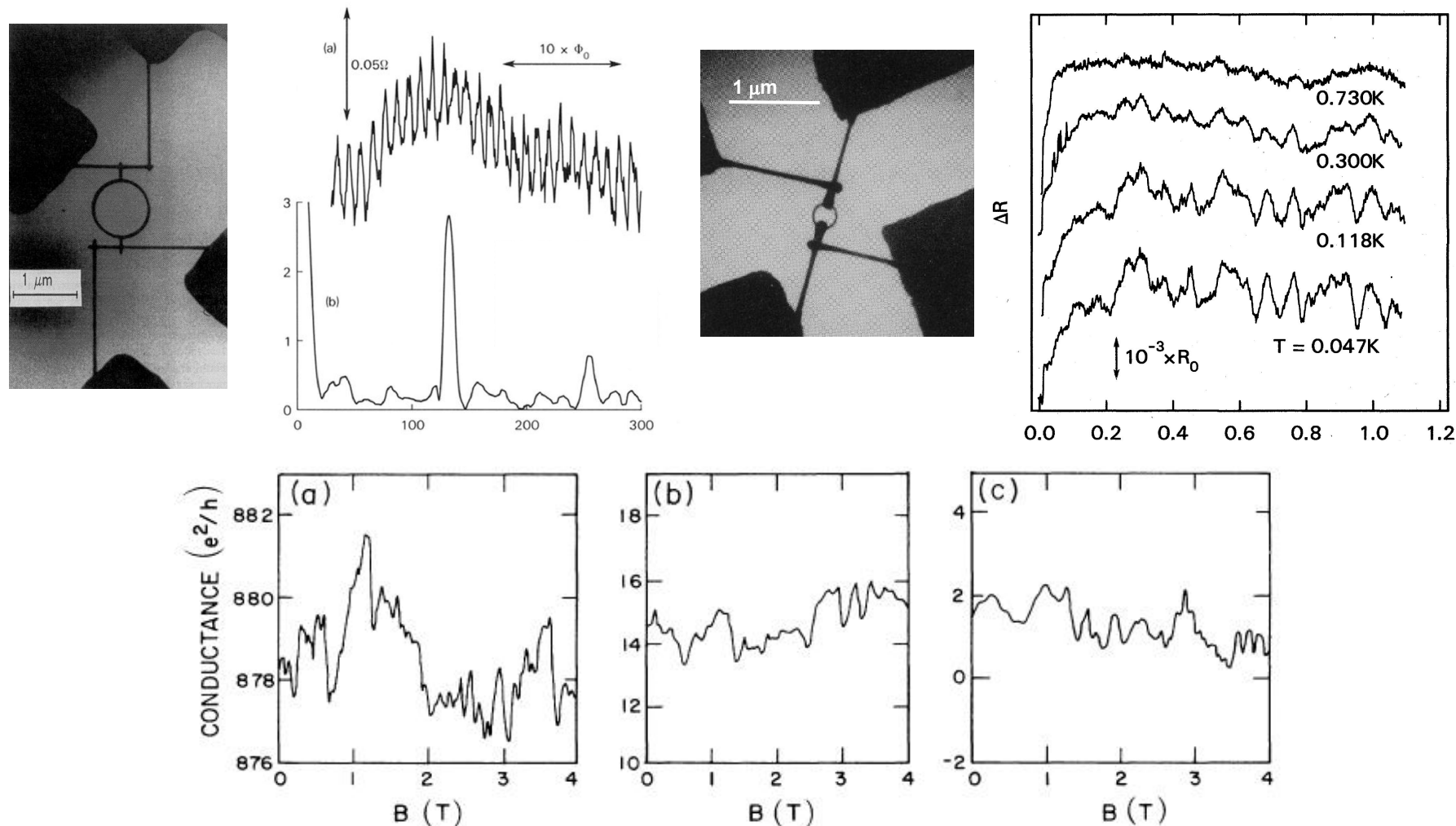


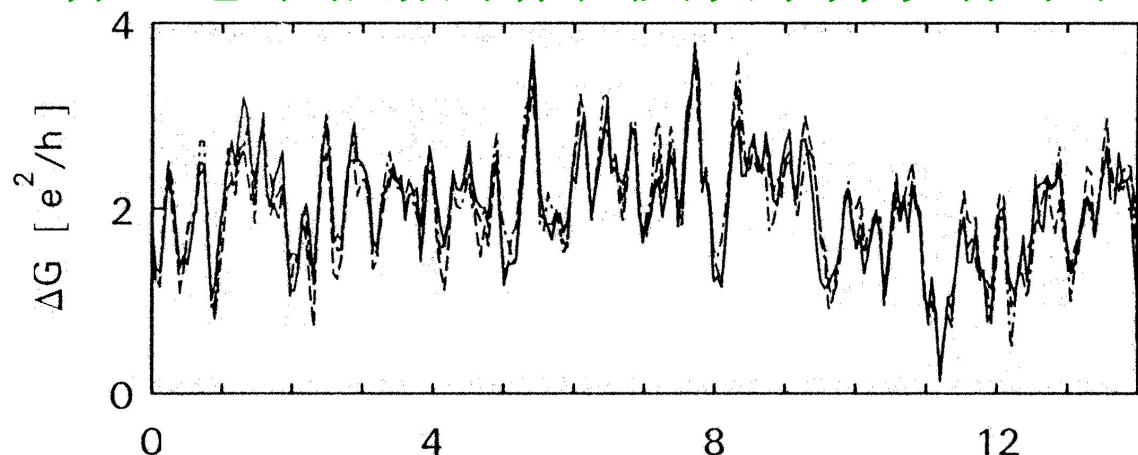
FIG. 1. Comparison of aperiodic magnetoconductance fluctuations in three different systems. (a) $g(B)$ in 0.8-μm-diam gold ring, analysis of data from Refs. 3 and 4, reprinted with the permission of Webb *et al.* (the rapid Aharonov-Bohm oscillations have been filtered out). (b) $g(B)$ for a quasi-1D silicon MOSFET, data from Ref. 9, reprinted with the permission of Skocpol *et al.* (c) Numerical calculation of $g(B)$ for an Anderson model using the technique of Ref. 11. Conductance is measured in units of e^2/h , magnetic field in tesla. Note the 3 order-of-magnitude variation in the background conductance while the fluctuations remain order unity.

(1)一般特征

- a. 与时间无关的非周期涨落，不是热噪声(和时间有关)。
- b. 这种涨落是样品特有的(sample-specific), 涨落花样可重复(pattern)。
- c. 涨落大小是 e^2/h 量级($\sim 4 \times 10^{-5} S$), 普适量。与样品的材料、尺寸、无序程度无关，与样品的形状和空间维度只有微弱的关系，只要求样品具有介观尺度，并处于金属区：即

$$\lambda_F \ll l \ll L \leq L_\phi \ll \xi$$

普适电导涨落的存在反映了介观体系和宏观体系本质上的差别

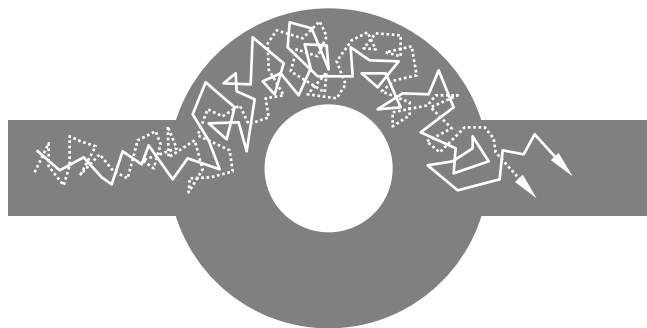


**REPRODUCIBILITY OF THE CONDUCTANCE
FLUCTUATIONS
MEASURED IN A GOLD RING**

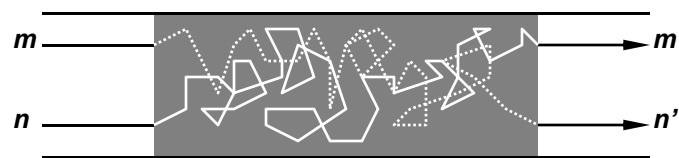
S. Washburn and R. A. Webb
Adv. Phys. 35, 375 (1986)

(2)物理解释

从样品一边到另一边的透射几率幅是许多通过样品的费曼路径相应的几率幅之和。在金属区电子通过样品时经历多次与杂质的散射，其费曼路径是无规行走式的准经典“轨道”，不同的费曼路径之间的相位差是不规则的→随机干涉效应 (Stochastic interference)，使电导呈现非周期的不规则涨落。



**INTERFERENCE BETWEEN TWO POSSIBLE
ELECTRON PATHS WHICH PROPAGATE
ALONG THE SAME ARM OF THE RING**



**TWO DIFFERENT TRANSMISSION PATHS
THROUGH A DISORDERED SAMPLE**

由统计力学，边长为L的宏观体系物理量x的相对涨落为：

$$\frac{\langle (\delta x)^2 \rangle}{\langle x \rangle^2} \approx \left(\frac{L_c}{L} \right)^d \quad \langle (\delta x)^2 \rangle \equiv \langle x^2 \rangle - \langle x \rangle^2$$

$\langle \dots \rangle$ 系综平均， L_c 是某一关联长度， d 是体系的维度
 $L \rightarrow \infty$ ， x 的相对涨落趋于零 $\rightarrow$ 经典自平均行为 (self-averaging)

对于普适电导涨落： $\langle (\delta G)^2 \rangle \approx \left(\frac{e^2}{h} \right)^2$

电导的平均值满足欧姆定律： $\langle G \rangle = \sigma L^{d-2}$

$$\frac{\langle (\delta G)^2 \rangle}{\langle G \rangle^2} \approx L^{4-2d}$$

$d < 4$ ，与经典自平均行为不符

$d = 2$ ，电导的涨落与尺度无关（限于介观体系，金属区）

$d = 1$ ，电导的相对涨落随 L 增加而增加。

(3)UCF的简单推导

考虑一介观金属导体，设其两端由理想导体相联，金属的电导：

$$G = \frac{e^2}{h} \sum_{\alpha, \beta=1}^{N_C} |t_{\alpha\beta}|^2 = \frac{e^2}{h} \sum_{\alpha, \beta=1}^{N_C} T_{\alpha\beta}$$

N_C ：总通道数目

$$N_C \approx (k_F L)^{d-1}$$

L ：导线的横向线度， d ：维度

第一步：求透射几率的涨落

$$t_{\alpha\beta} = \sum_{i=1}^{N_p} A_{\alpha\beta}(i)$$

$A_{\alpha\beta}(i)$ 代表经过第 i 条费曼路径从 α 通道到 β 通道的几率

N_p 为费曼路径的总数， $N_p \gg 1$

假设 $A_{\alpha\beta}(i)$ 彼此独立： $A_{\alpha\beta}(i) = \sqrt{W_i} e^{i\phi_i}$

W_i 是费曼路径相应的经典传播几率， ϕ_i 为位相

$$T_{\alpha\beta} = |t_{\alpha\beta}|^2 = \left| \sum_i \sqrt{W_i} e^{i\phi_i} \right|^2 = \sum_{ij} \sqrt{W_i W_j} \cos(\phi_i - \phi_j) = \sum_i W_i + \sum_{i \neq j} \sqrt{W_i W_j} \cos(\phi_i - \phi_j)$$

取系综平均，忽略弱局域化效应：

$$\langle T_{\alpha\beta} \rangle = \left\langle \sum_i W_i \right\rangle, \text{透射几率的系综平均近似等于经典几率}$$

$$\text{透射几率的方差: } \langle (\delta T_{\alpha\beta})^2 \rangle = \langle (T_{\alpha\beta} - \langle T_{\alpha\beta} \rangle)^2 \rangle = \langle T_{\alpha\beta}^2 \rangle - \langle T_{\alpha\beta} \rangle^2$$

当计算透射几率的平方平均时，量子干涉起作用：

$$\begin{aligned} T_{\alpha\beta}^2 &= \left(\sum_{i,j} \sqrt{W_i W_j} \cos(\phi_i - \phi_j) \right)^2 = \sum_{ijkl} \sqrt{W_i W_j W_k W_l} \cos(\phi_i - \phi_j) \cos(\phi_k - \phi_l) \\ &= \sum_{ij} W_i W_j + 2 \sum_{i \neq j} W_i W_j \cos^2(\phi_i - \phi_j) + 2 \sum_{i \neq j, k} \sqrt{W_i W_j W_k} \cos(\phi_i - \phi_j) \\ &\quad + \sum_{(i \neq j) \neq (k \neq l)} \sqrt{W_i W_j W_k W_l} \cos(\phi_i - \phi_j) \cos(\phi_k - \phi_l) \end{aligned}$$

取系综平均：③，④两项均等于零 $\langle \cos^2(\phi_i - \phi_j) \rangle = \frac{1}{2}$

$$\text{②项} = \sum_{i \neq j} W_i W_j = \sum_{ij} W_i W_j - \sum_i W_i^2 \approx \sum_{ij} W_i W_j$$

在介观导体， W_i 基本相等，为 $1/N_p$ 小量

$$\langle T_{\alpha\beta}^2 \rangle \cong 2 \left\langle \sum_{ij} W_i W_j \right\rangle \cong 2 \left\langle \sum_i W_i^2 \right\rangle = 2 \langle T_{\alpha\beta} \rangle^2$$

量子干涉效应导致 $\langle T_{\alpha\beta}^2 \rangle$ 与 $\langle T_{\alpha\beta} \rangle^2$ 之间的区别，从而导致介观涨落：

$$\frac{\sqrt{\langle (\delta T_{\alpha\beta})^2 \rangle}}{\langle T_{\alpha\beta} \rangle} \cong 1$$

透射几率的相对涨落的量级为100%

第二步：求电导G的涨落

$$\langle G \rangle = \frac{e^2}{h} \sum_{\alpha, \beta=1}^{N_c} \langle T_{\alpha\beta} \rangle$$

$$\langle (\delta G)^2 \rangle = \langle (G - \langle G \rangle)^2 \rangle = \left(\frac{e^2}{h} \right)^2 \sum_{\alpha\beta} \sum_{\alpha'\beta'} \langle (T_{\alpha\beta} - \langle T_{\alpha\beta} \rangle) \times (T_{\alpha'\beta'} - \langle T_{\alpha'\beta'} \rangle) \rangle$$

该式的结果与不同通道的透射几率是否存在关联有关

$\alpha \rightarrow \beta$, $\alpha' \rightarrow \beta'$, 透射路径不存在关联:

$$\langle (\delta G_u)^2 \rangle = \left(\frac{e^2}{h} \right)^2 \sum_{\alpha\beta} \langle (T_{\alpha\beta} - \langle T_{\alpha\beta} \rangle)^2 \rangle = \left(\frac{e^2}{h} \right)^2 \sum_{\alpha\beta} \langle (\delta T_{\alpha\beta})^2 \rangle = \left(\frac{e^2}{h} \right)^2 \sum_{\alpha, \beta=1}^{N_c} \langle T_{\alpha\beta} \rangle^2$$

在金属区，不同通道的透射几率近似相同：

$$\sqrt{\langle (\delta G_u)^2 \rangle} \approx \frac{e^2}{h} N_c \langle T_{\alpha\beta} \rangle$$

由欧姆定律： $\langle G \rangle = \sigma L^{d-2}$ $\sigma = \frac{e^2}{h} k_F^{d-1} l$ $\rightarrow$ $\langle G \rangle = \frac{e^2}{h} N_c \frac{l}{L}$

$\longrightarrow \langle T_{\alpha\beta} \rangle = \frac{1}{N_c} \cdot \frac{l}{L} \longrightarrow \sqrt{\langle (\delta G_u)^2 \rangle} = \frac{e^2}{h} \cdot \frac{l}{L}$ 与UCF不同！

放弃不同通道透射互不关联的假定，用反射几率来推导

定义： $R \equiv \frac{e^2}{h} \sum_{\alpha, \beta=1}^{N_C} |r_{\alpha\beta}|^2$ $|r_{\alpha\beta}|^2$ 代表从 α 到 β 通道的反射几率

$$\sum_{\beta} (|t_{\alpha\beta}|^2 + |r_{\alpha\beta}|^2) = 1 \quad R + G = \frac{e^2}{h} \sum_{\alpha\beta} (|t_{\alpha\beta}|^2 + |r_{\alpha\beta}|^2) = \frac{e^2}{h} N_C$$

G, R之间相差一个常数 $\longrightarrow \langle (\delta G)^2 \rangle = \langle (\delta R)^2 \rangle$

类似 $|t_{\alpha\beta}|^2$ ，反射几率的涨落： $\sqrt{\langle (\delta |r_{\alpha\beta}|^2)^2 \rangle} \approx \langle |r_{\alpha\beta}|^2 \rangle$

假定 $|r_{\alpha\beta}|^2$ 与 $|r_{\alpha'\beta'}|^2$ 互不关联： $\sqrt{\langle (\delta R)^2 \rangle} = \frac{e^2}{h} N_C \langle |r_{\alpha\beta}|^2 \rangle$

$$\langle |r_{\alpha\beta}|^2 \rangle = \frac{1}{N_C} (1 - \frac{l}{L}) \cong \frac{1}{N_C} \Rightarrow \sqrt{\langle (\delta G)^2 \rangle} = \sqrt{\langle (\delta R)^2 \rangle} \cong \frac{e^2}{h}$$

原因：反射过程有可能主要由少数几次散射的过程决定，而透射过程必须经历多次散射。

(4)移动一个杂质所引起的电导涨落

电子量子干涉—依赖于不同的费曼路径→杂质位形对电导涨落有较大影响。

$T=0K$ ，使一个杂质移动距离 $\delta r > k_F^{-1}$

样品电导的涨落： $\sqrt{\langle (\delta G_1)^2 \rangle} \cong \begin{cases} \frac{e^2}{h}, d=1 \\ \frac{e^2}{h}, d=2 \\ \frac{e^2}{h} \left(\frac{l}{L}\right)^{\frac{1}{2}}, d=3 \end{cases}$

“牵一发而动全身”

对一，二维情形，移动一个杂质的效果与移动全体杂质的效果相当样

简单分析：边长L的立方体，考虑一条典型费曼路径

按Einstein关系： $L = \sqrt{D \cdot \Delta t}$ $\Delta t = N_s \tau$ $N_s = \frac{L^2}{D \tau}$

$D = v_F \frac{l}{d}$ $l = v_F \tau$ $\longrightarrow$ $N_s \approx L^2 / l^2$

一条费曼路径的体积： 每一步的平均步长 l ，截面积 $\sim k_F^{-(d-1)}$

$V_1 \sim \left(\frac{L}{d}\right)^2 l \cdot k_F^{-(d-1)}$

它与样品总体积 $V_d = L^d$ 之比：
$$f = \frac{V_1}{V_d} \sim \frac{1}{(k_F l)^{d-1}} \left(\frac{L}{l} \right)^{2-d}$$

令 n_i 代表样品中杂质浓度，则：
$$f = \frac{V_1}{V_d} = \frac{V_1 n_i}{V_d n_i} = \frac{N_1}{N_t}$$

一条典型的费曼路径所通过的杂质数在总杂质数中所占的百分比，等价于通过特定杂质的费曼路径数在总费曼路径数中所占百分比。因此，移动一个杂质相当于改变了所有费曼路径中百分比为 f 的费曼路径。

在费曼路径独立的情形下：
$$\sqrt{\langle (\delta G_1)^2 \rangle} \cong f^{\frac{1}{2}} \sqrt{\langle (\delta G)^2 \rangle} = \frac{e^2}{h} f^{\frac{1}{2}}$$

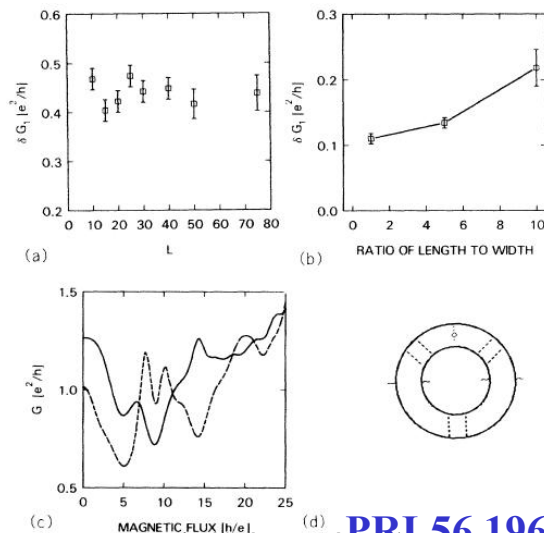


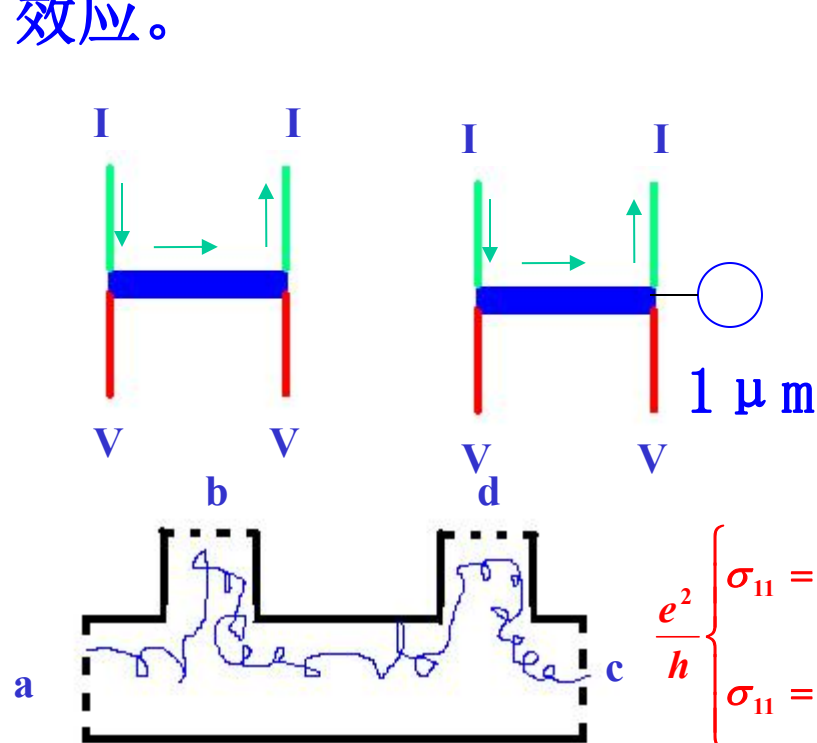
FIG. 1 (a) The rms deviation of the conductance (in units of e^2/h) of an $L \times L$ Anderson model ($W/V=4$) upon interchange of the local energy of two sites. The rms deviation for a complete configuration change is 0.86 (Ref. 5). (b) δG_1 of an $M \times L$ Anderson model ($M=25$, $W/V=1$) as the site energy of a single site is changed by $W/2$ plotted vs the aspect ratio L/M . (c) $G(B)$ for 40×40 Anderson model vs B in units of h/e normal to the sample. Solid and dashed curves correspond to impurity configurations which differ only by the interchange of a pair of sites. (d) A typical diagram that contributes to $(\delta G_1)^2$. Dashed lines denote impurity averaging and the diamond denotes the vertex [Eq.

4. 非定域效应(非局域性电导)

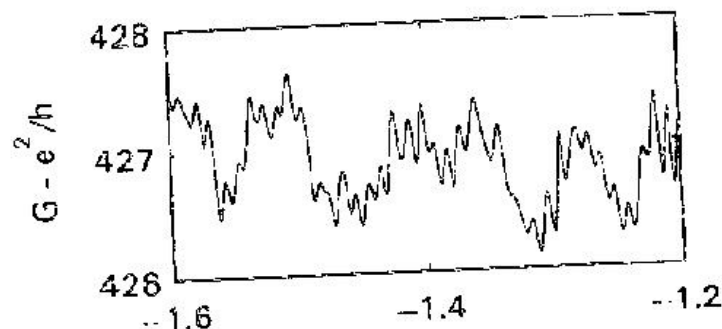
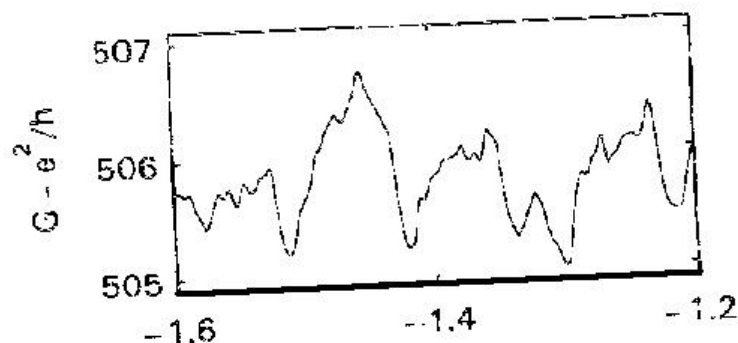
对 $0.1\ \mu\text{m}$ 的结构加上1V电压， $E \sim 10^5\text{V/cm}$

导电机理已不能用普通的线性理论描述，而必须考虑非线性效应。

电子自由程接近或超过样品尺寸，关联效应可遍及整个样品。结构和结构，元件和元件之间的距离大为缩短，很难用单个分立元件的观点来进行分析，必须考虑元件之间的相干性和合作效应。



$$\frac{e^2}{h} \left\{ \begin{aligned} \sigma_{11} &= \frac{I_{ac}}{V_{bd}} \\ \sigma_{11} &= \frac{I_{bd}}{V_{ac}} \end{aligned} \right.$$



5. 正常金属环中的持续电流

在介观尺寸的一维非超导金属环中，也可能通过磁场诱导持续电流。

计算平衡态下的持续电流的热力学公式：

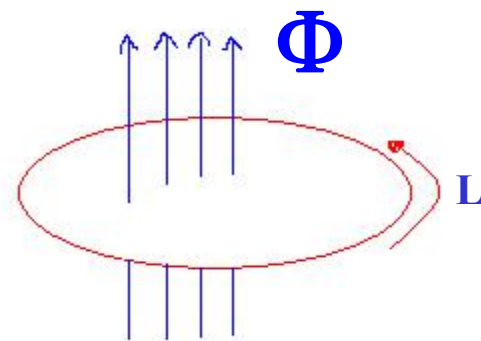
$$I(\phi) = -C \frac{\partial F(\phi)}{\partial \phi} \quad F: \text{自由能}$$

$$T = 0K, I = -C \frac{\partial E(\phi)}{\partial \phi} = -C \sum_{E_n < E_F} \frac{\partial E_n(\phi)}{\partial \phi} = \sum_{E_n < E_F} I_N$$

$$E_n(\phi) = \frac{\hbar^2 k_n^2}{2m} = \frac{4\pi^2 \hbar^2}{2mL^2} \left(n + \frac{\phi}{\phi_0}\right)^2$$

$E_n(\phi)$ 是 ϕ 的偶函数，以 ϕ_0 为周期。

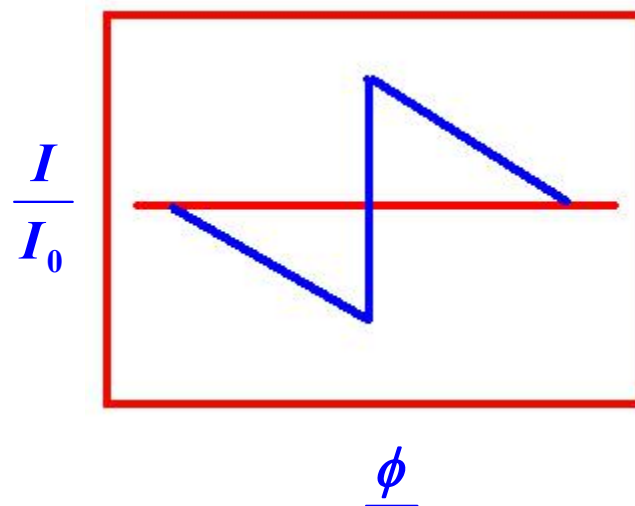
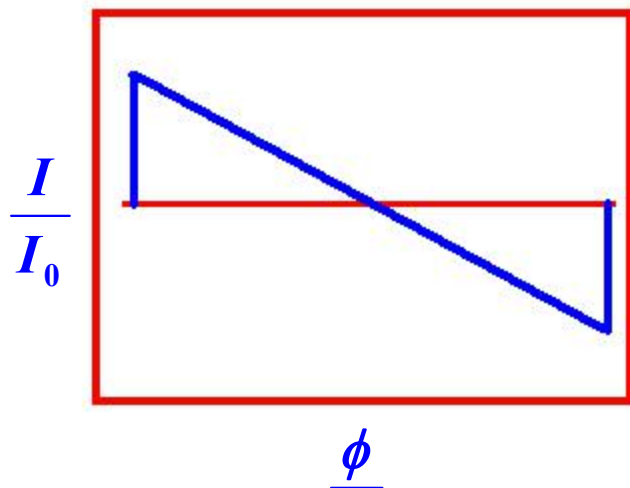
$I(\phi)$ 是 ϕ 的奇函数，对相邻能级，曲率的斜率正负相反



对一维环且没有无序， $T=0K$ 时总电流的大小与符号由最高占据能级的电流决定。

总电子数 $N=$ 奇，
$$I(\phi) = -I_0 \frac{2\phi}{\phi_0}, \quad I_0 = ev_F / L \quad -0.5 < \frac{\phi}{\phi_0} < 0.5$$

总电子数 $N=$ 偶，
$$I(\phi) = \begin{cases} I_0 \left(1 - 2 \frac{\phi}{\phi_0} \right), & 0 \leq \frac{\phi}{\phi_0} \leq 0.5 \\ -I_0 \left(1 + 2 \frac{\phi}{\phi_0} \right), & -0.5 \leq \frac{\phi}{\phi_0} < 0 \end{cases}$$



将电流展成Fourier级数：

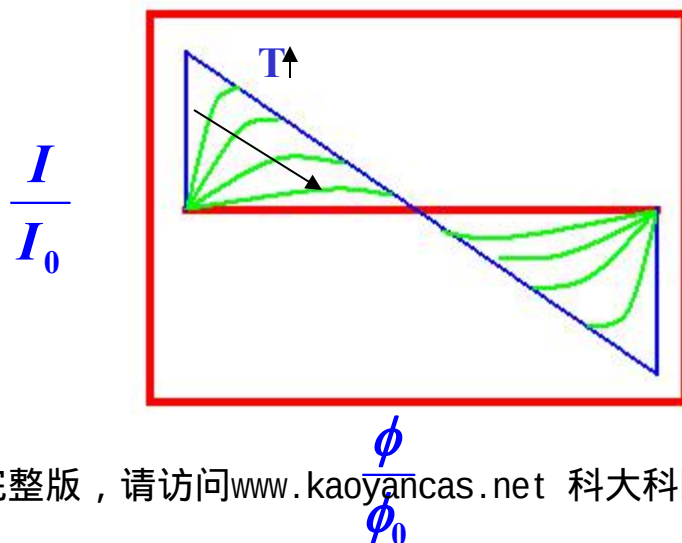
$$I(\phi) = \frac{2I_0}{\pi} \sum_{l=1}^{\infty} \frac{1}{l} \cos(lk_F L) \sin\left(2\pi l \frac{\phi}{\phi_0}\right), \quad N = k_F L / \pi$$

电流的第 l 次谐波的振幅为 $\frac{2I_0}{\pi l} \cos(lk_F L)$ ，周期为 $\frac{\phi_0}{l}$

重要的为最低阶谐波。 $l = 1, 2$ 的谐波，周期为 $\phi_0, \phi_0 / 2$

$T \neq 0 K$:

$$I(\phi) = \sum_n I_n(\phi) f(E_n - \mu) = -c \sum_n \frac{\frac{\partial E_n}{\partial \phi}}{e^{\frac{E_n - \mu}{k_B T}} + 1}$$



多环实验结果与理论比较时，涉及系综平均问题。(T=0K)

(1). 变型正则系综(Modified canonical ensemble)

$N \gg 1$ 个彼此独立的环，每个环的总电子数固定不变，但不同的环除总电子数可以不同外，其他参数(如 ϕ, L) 均相同。

$$\langle I_N(\phi) \rangle_N \equiv \frac{1}{N} \sum_{i=1}^N I_{N_i}(\phi), \quad I_{N_i}(\phi): \text{总电子数为 } N_i \text{ 的环的电流}$$

$$I_N(\phi) = \frac{2I_0}{\pi} \sum_{l=1}^{\infty} \frac{1}{l} \cos(lk_F L) \sin\left(2\pi l \frac{\phi}{\phi_0}\right), \quad k_F = \pi N / L$$

$$\langle \cos(lk_F L) \rangle_N = \langle \cos(l\pi N) \rangle_N = \begin{cases} 0, & \text{当 } l = 1, 3, 5, \dots, \text{奇数} \\ 1, & \text{当 } l = 2, 4, 6, \dots, \text{偶数} \end{cases}$$

$$\langle I_N(\phi) \rangle_N = \langle I_N^{(2)}(\phi) \rangle_N + \langle I_N^{(4)}(\phi) \rangle_N + \dots$$

对不同总电子数的系综的平均

(2). 变型巨正则系综 (Modified grand canonical ensemble)
不同环的化学势可以不同，其他参数均相同。

$$\langle I_{\mu}(\phi) \rangle_{\mu} \equiv \frac{1}{N} \sum_{i=1}^N I_{\mu_i}(\phi), \quad I_{\mu_i}(\phi): \text{化学势为 } \mu_i \text{ 的环的电流}$$

$$k_F = \frac{\sqrt{2m\mu}}{\hbar} \text{ 可连续变化: } \langle \cos(lk_F L) \rangle_{\mu} = 0$$

$$\langle I_{\mu}(\phi) \rangle_{\mu} = 0$$

对不同化学势的系综的平均

$$\langle I_N(\phi) \rangle_N \neq \langle I_{\mu}(\phi) \rangle_{\mu}$$

3.2 纳米体系

(1).纳米体系物理学(2).纳米化学(3).纳米材料学(4).纳米生物学
(5).纳米电子学(6).纳米加工学(7).纳米力学

1. 纳米结构单元

零维：团簇、量子点、纳米粒子

一维：纳米线、量子线、纳米管、纳米棒

二维：纳米带、二维电子气、超薄膜、多层膜、超晶格

体系的某个或数个特征长度在nm量级

2. 纳米结构的自技术

(1). 球磨和机械合金化工艺和技术(2). 化学合成工艺和技术
(3). 等离子电弧合成技术(4). 电火花制备技术(5). 激光合成技术
(6). 生物学制备技术(7). 磁控溅射技术(8). 燃烧合成技术
(9) 喷雾合成技术.....

Bottom-up, Top-down

3. 纳米体系的基本物理效应

(1). 小尺寸效应：尺寸与光波波长、德布罗意波长以及相干长度等相当或更小时，导致声、光、电磁、热力学等物性呈现新的小尺寸效应。

(2). 表面效应：

d(nm)	N	表面(%)
10	30,000	20
4	4,000	40
2	250	80
1	30	99

(3). 量子尺寸效应：
$$n = \frac{N}{V} \text{ 不变, } \varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{\frac{2}{3}} \quad g(\varepsilon_F) = \frac{3}{2} \frac{n}{\varepsilon_F}$$
$$\delta = \frac{2}{g(\varepsilon_F)V} = \frac{4}{3} \frac{\varepsilon_F}{N} \rightarrow \delta \sim \frac{1}{d^3} \quad T=1K, d=14nm$$
$$\delta > k_B T : \text{出现量子尺寸效应}$$

(4). 宏观量子隧道效应：

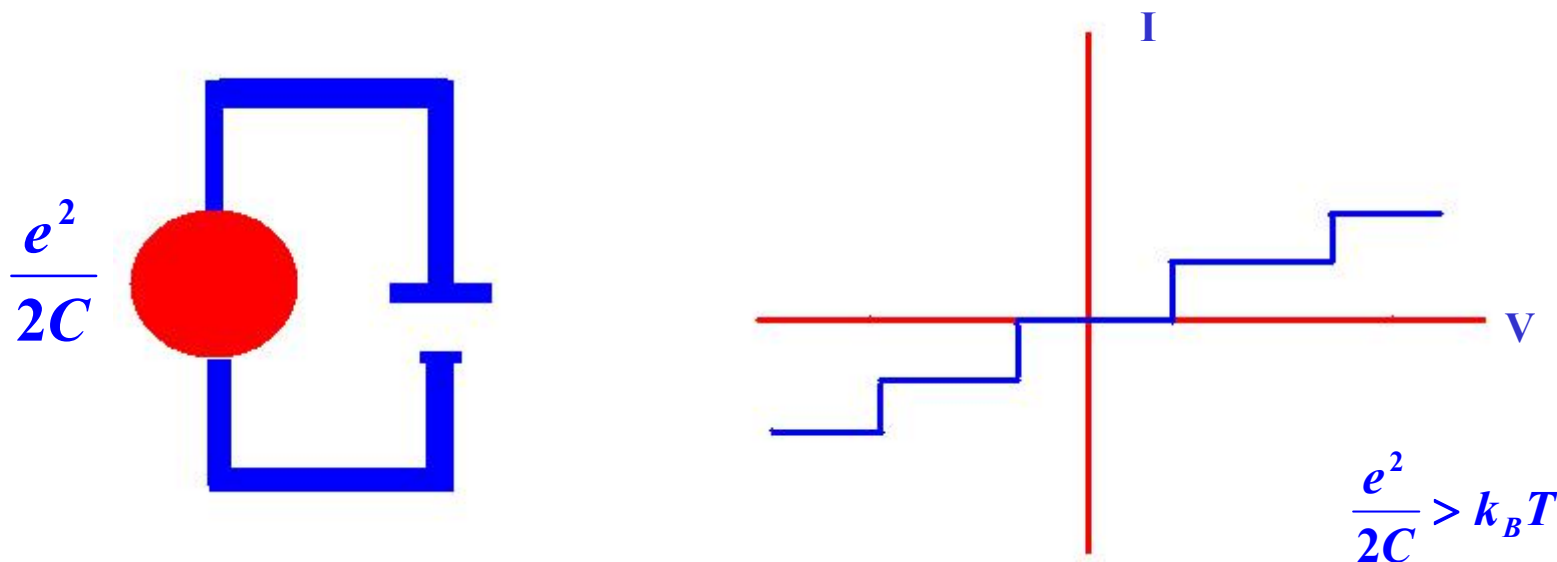
微观粒子具有贯穿势垒的能力。

宏观量：微颗粒的磁化强度，量子相干器件中的磁通量，亦具有隧道效应。

Fe-Ni 薄膜中畴壁运动速度在低于某一临界温度时基本上与温度无关。

限定了磁带、磁盘进行信息储存的时间极限。

(5). 库仑阻塞与库仑台阶效应：



(6). 介电限域效应:

纳米微粒分散在异质介质中由于界面引起的体系介电增强现象。

纳米粒子的光吸收带边移动(蓝移, 红移)的Brus公式:

$$E(r) = E_g(r = \infty) + \frac{h^2 \pi^2}{2\mu r^2} - 1.786 \frac{e^2}{\epsilon r} - 0.248 E_{Ry}$$

$E(r)$: 纳米粒子的吸收带隙, r : 粒子半径

$$\mu = \left[\frac{1}{m_e} + \frac{1}{m_h} \right]^{-1} : \text{折合质量}$$

第二项: 量子限域能 (蓝移)

第三项: 介电限域效应 (红移)

第四项: 有效里德堡能

4. 纳米材料的奇特物性

(1). 热学性能

纳米粒子的熔点、开始烧结温度和晶化温度均比常规粉体的低得多。(表体比大)

(2). 磁学性质

(a). 超顺磁性 超顺磁性：矫顽力 $H_c \rightarrow 0$ ，对于 $\frac{\mu H}{k_B T} \ll 1$ 时：

$$\text{磁化强度： } M_p \approx \frac{\mu^2 H}{3k_B T}, \quad \mu \text{ 为粒子磁矩}$$

起源：在小尺寸下，当各向异性能减少到与热运动能可相比拟时，磁化方向就不再固定在一个易磁化方向，易磁化方向作无规律的变化，结果导致超顺磁性的出现。

(b). 矫顽力

纳米粒子尺寸高于超顺磁临界尺寸时通常呈现高的矫顽力

每个粒子是一个单磁畴

(c). 居里温度

居里温度 T_c 与交换积分 J 成正比，并与原子构形和间距有关。纳米粒子的 T_c 比固体相应的低。

纳米粒子中原子间距随着颗粒尺寸减少而减小。原子间距小将会导致 J 的减小，因而 T_c 下降。

5nm Ni: 点阵参数缩小2.4%

(d). 磁化率

纳米粒子的磁性与它所含的总电子数的奇偶性密切相关。电子数为奇数的磁化率服从：

居里—外斯定律：
$$\chi = \frac{C}{T - T_c}$$

量子尺寸效应使磁化率遵从 d^{-3} 规律 (d 平均颗粒直径)

电子数为偶数的磁化率服从：
$$\chi \propto k_B T$$

磁化率遵从 d^2 规律

(3). 光学性质

(a). 宽频带强吸收

(b). 蓝移和红移现象

量子限域效应：蓝移

表面效应：红移

(c). 量子限域效应

激子带的吸收系数随粒径下降而增加，即出现激子增强吸收并蓝移

(d). 纳米粒子的发光

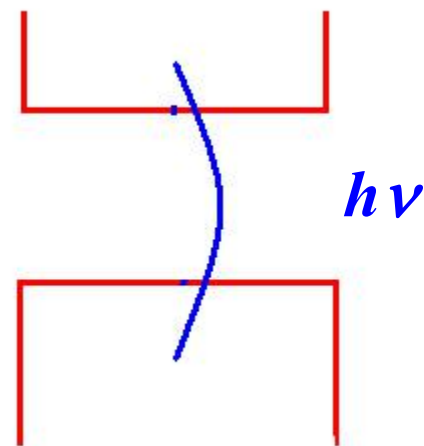
(4). 表面活性及敏感特性

Au纳米团簇的催化 ($\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$)

(5). 光催化性能

纳米半导体独特性能

nano-TiO₂:



3.3 原子团簇

原子团簇：几个，几十个，成千上万的原子的聚合体。
 $0.1\text{nm} \sim 10\text{nm}$

性质既不同于单个原子、分子，也不同于固体或液体

王广厚<<团簇物理的新进展>>
<<物理学进展>>1994年6月，1998年3月

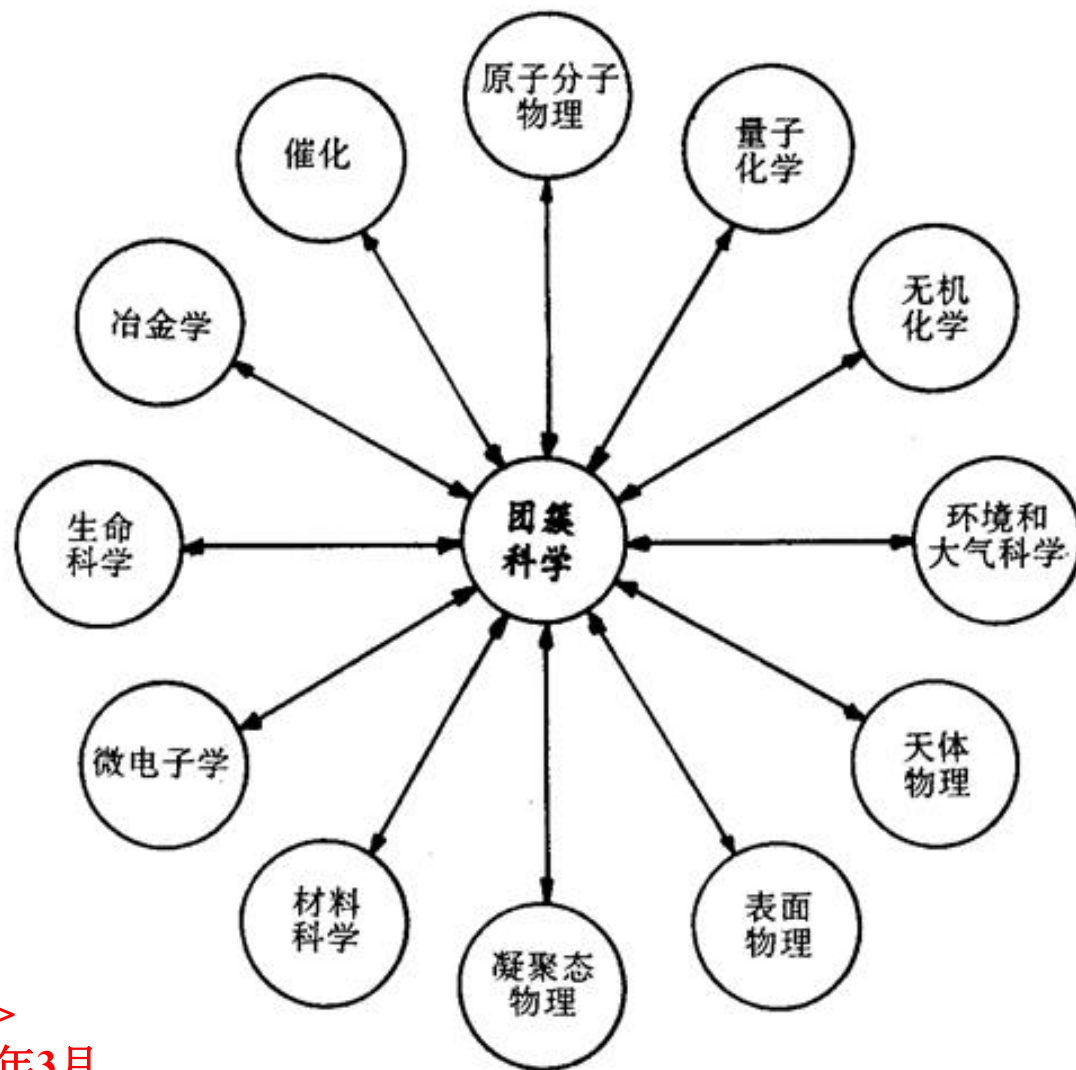
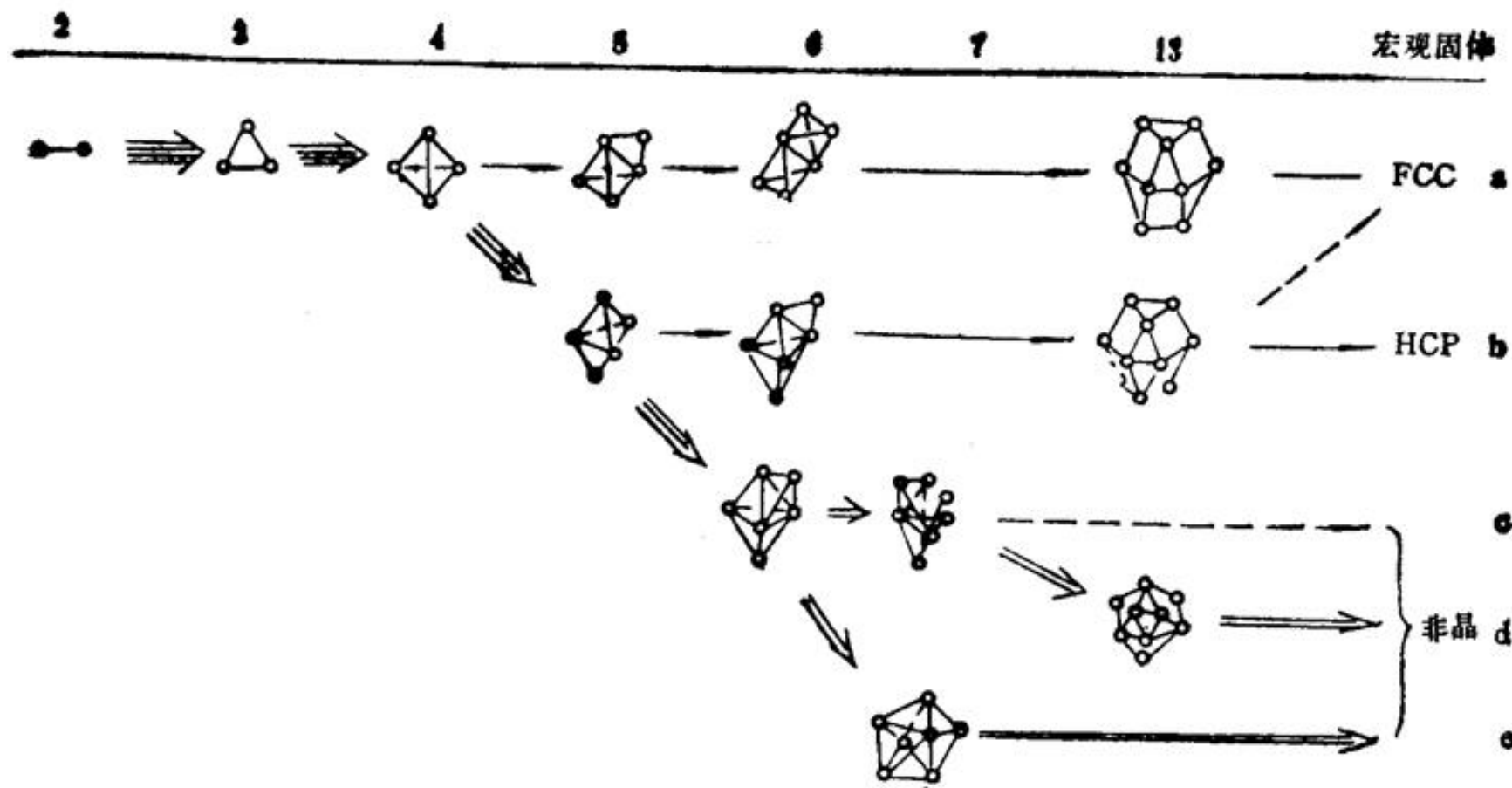


图1 团簇科学同一些科学领域的相互关系

1. 团簇研究的基本问题：

弄清团簇如何由原子、分子一步一步发展而成，以及随着这种发展，团簇的结构和性质如何变化。



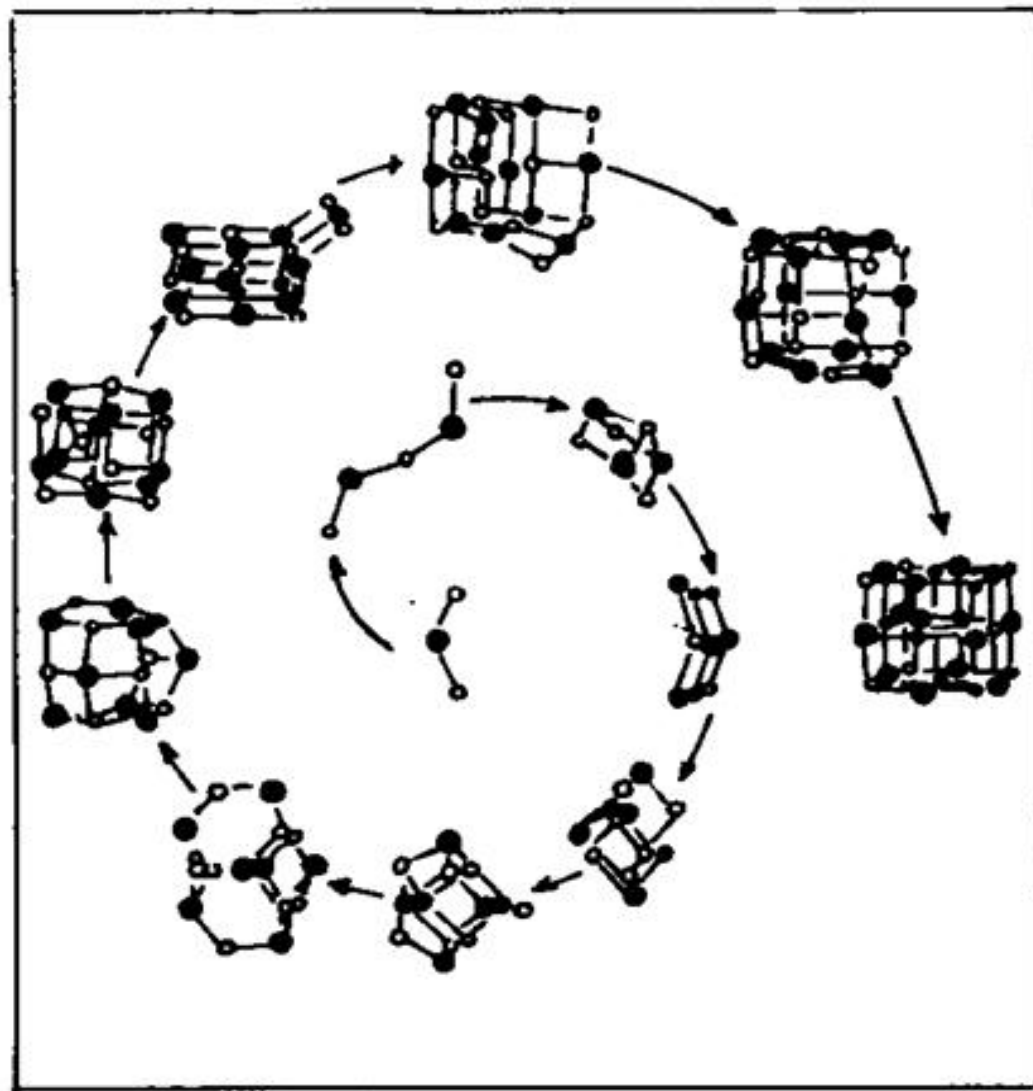


图 1 氯化钠团簇 $\text{Na}^+(\text{NaCl})_n$ 最初十三步生长螺旋(理论模型计算)。

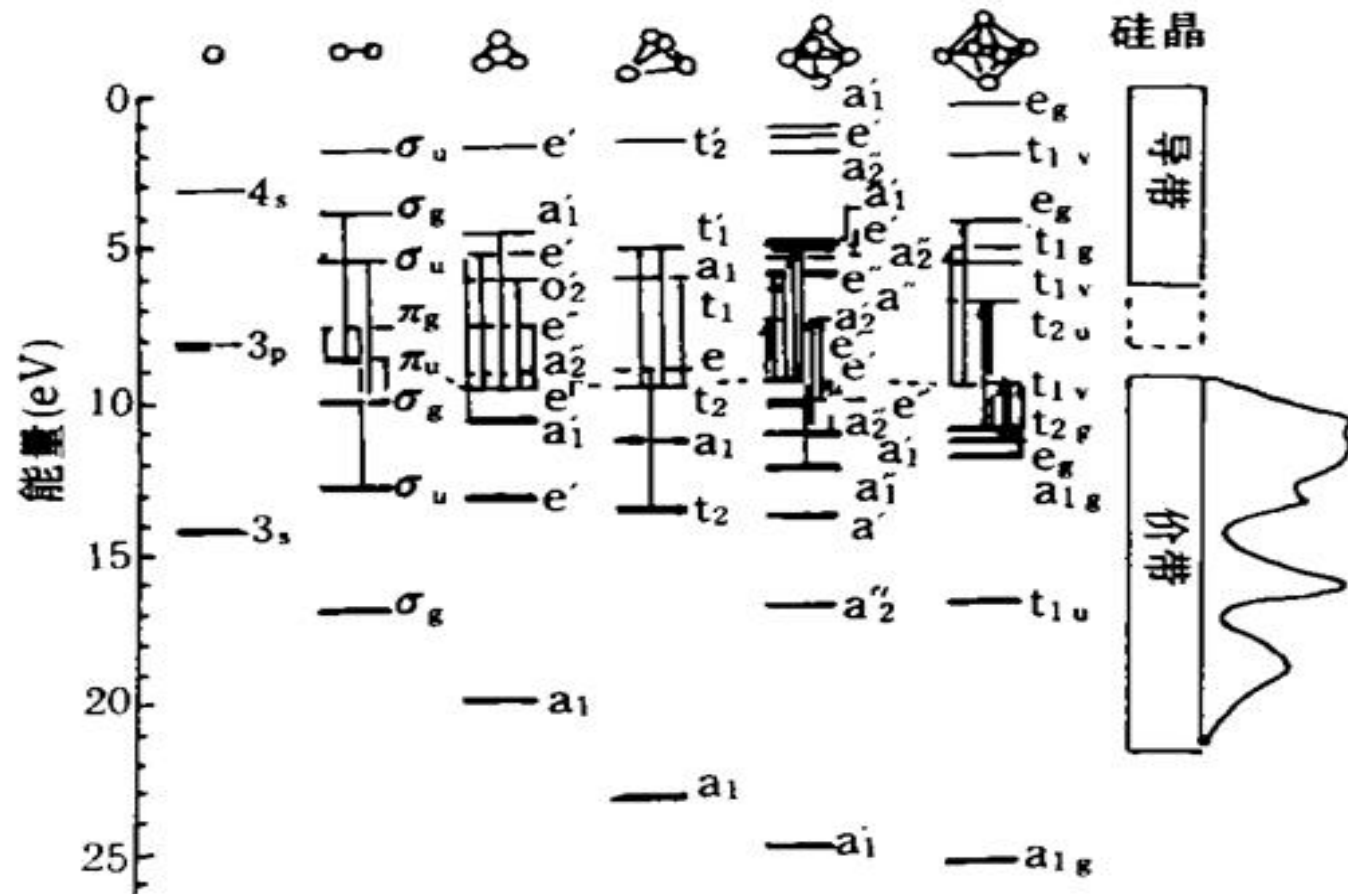


图 2 硅团簇的电子能级图。理论计算是采用黑格尔(Hückel)近似并取团簇有一定结构。

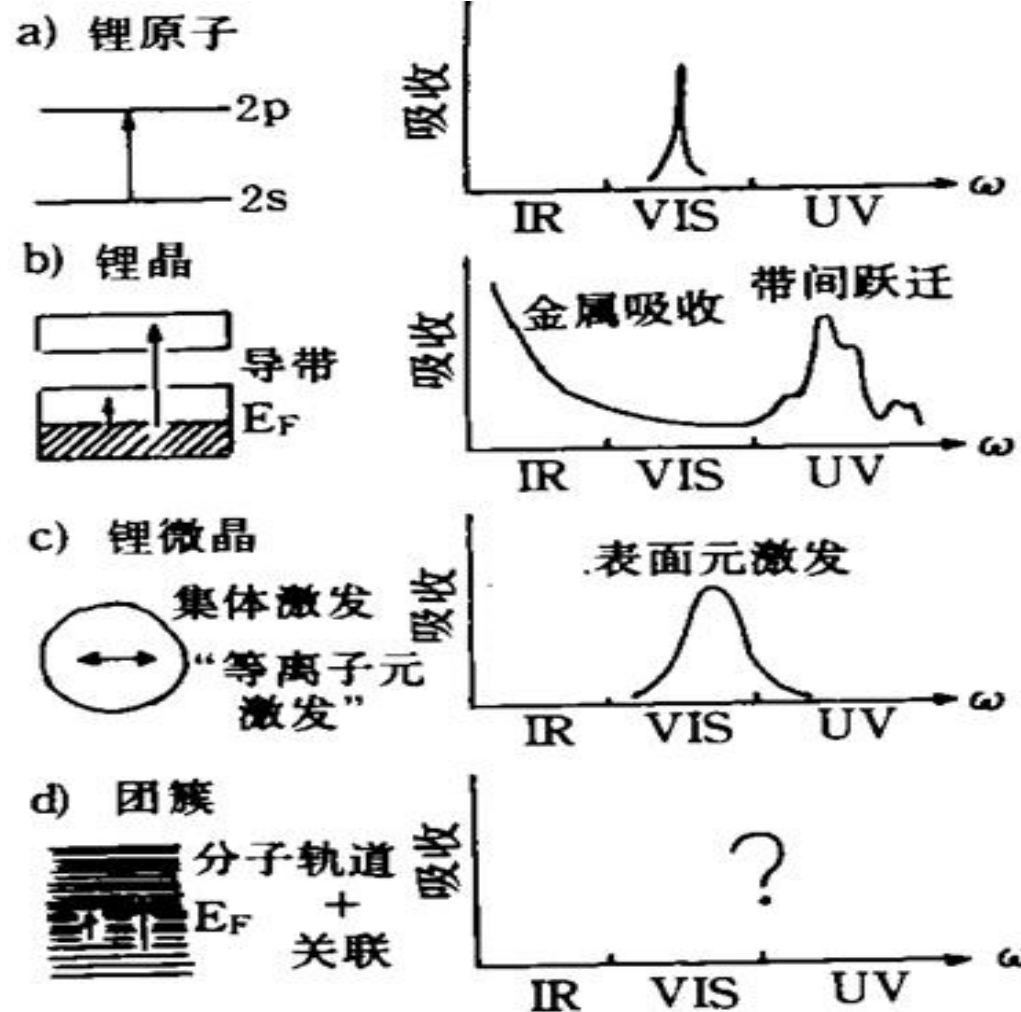


图 3 锂在各种不同聚集阶段对光的吸收特征：(a)锂原子，(b)锂晶，(c)含有 500 个锂原子的微晶，(d)锂团簇。

2. 团簇的产生与检测

物理制备法和化学合成法

真空、气相和凝聚相合成(生成条件)

物理方法：溅射、热蒸法和激光蒸发等产生原子气，通过绝热气体膨胀或惰性气体冷凝得到中性团簇，再用各种方法使之电离，包括：电子电离、光电离和离子反应等。

团簇电离后可通过四极谱仪、静电或磁谱仪，以及飞行时间质谱仪(TOF)探测。

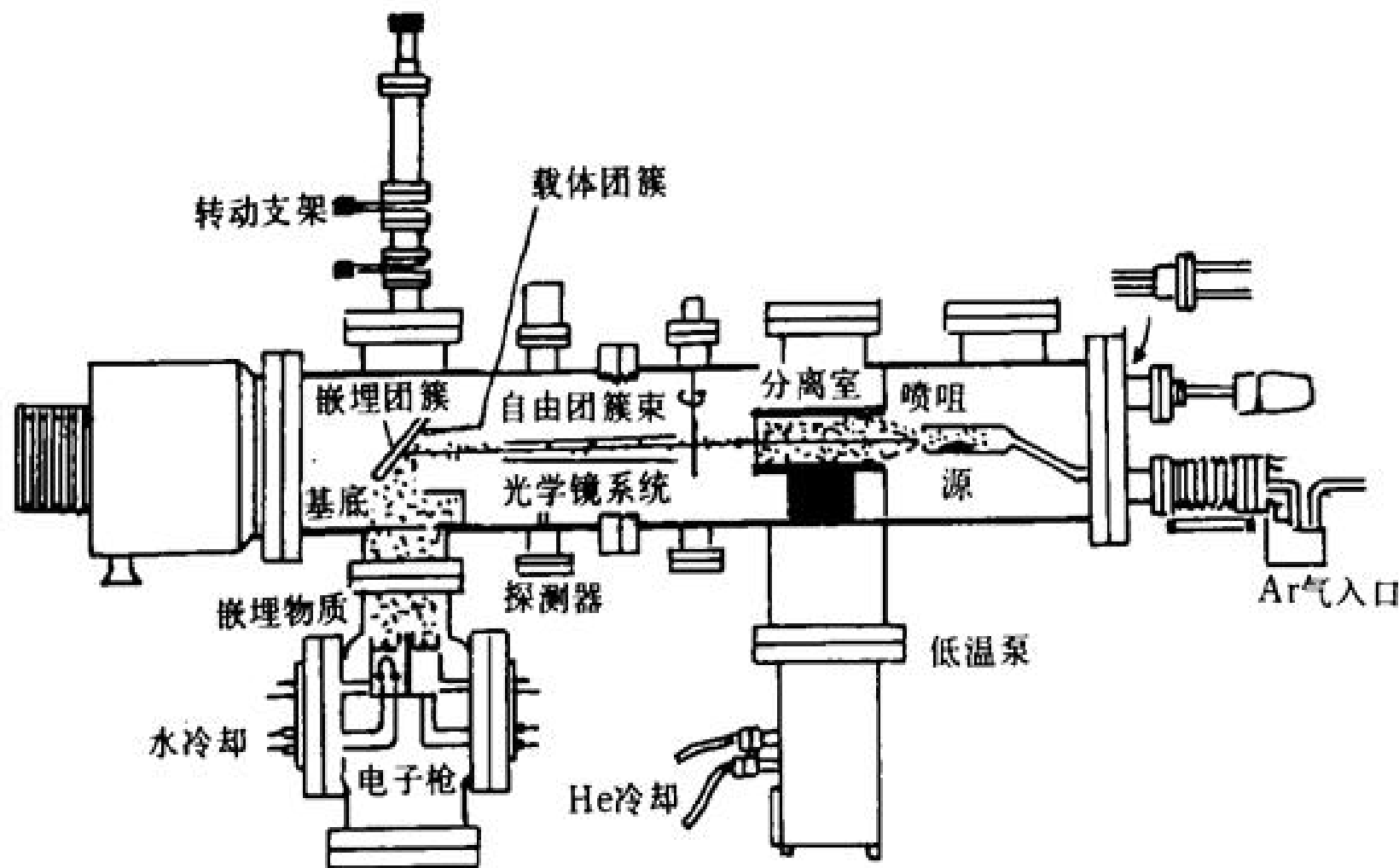


图 4 用于研究自由,载体和嵌入团簇的实验装置。

3. 团簇的稳定结构和幻数

原子中的电子状态

原子核中的核子状态

幻数特征（壳层结构）

原子团簇？ YES

团簇的幻数序列与构成团簇的原子键合方式有关：

金属键：自由价电子

共价键：Si, C

离子键：金属卤化物

范德瓦尔斯键：惰性元素

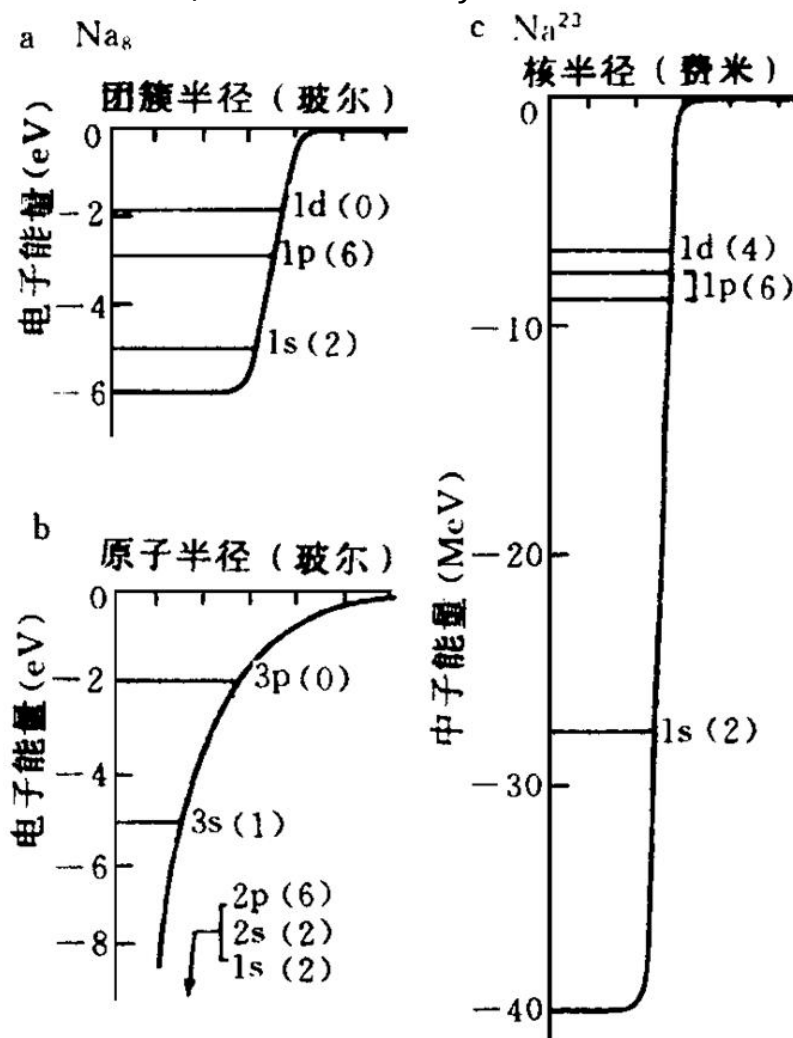


图 1 三种费米子体系的势阱和能级图:

a) Na_8 原子团簇 b) 钠原子和 c) Na^{23}

原子核

团簇结构中的序：

(a) 位置序是经典粒子的特征

(b) 动量序则是德布罗依波的特征

$$\text{平均热能: } \frac{3}{2} k_B T \quad \text{粒子动能: } \frac{1}{2} m v^2$$

$$\text{粒子间距 } a \sim \lambda = \frac{h}{mv} \Rightarrow T_0 \equiv \frac{h^2}{3mk_B a^2}$$

$T > T_0$: 德布罗依波长小于原子 之间间距

团簇内粒子的位置序占 主导地位

$T < T_0$: 德布罗依波长大于原子 之间间距

团簇内动量序或波序占 主导地位

一般金属原子: $T_0 \approx 60 K$ 轻元素 (He 等): $T_0 \approx 5 K$

(1). 惰性元素团簇—Mackay二十面体

位置序起主导作用 (Ar, Kr, Xe...)

Lennard - Jones 相互作用势：
$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$$

$$H = \sum \frac{p^2}{2m} + \frac{1}{2} \sum_{i \neq j} V(|r_i - r_j|)$$

在零温度近似下，系统 能量是：

$$E = \sum_{i=1}^{n-1} \sum_{j=i+1}^n V(|r_i - r_j|)$$

最佳结构： *Mackay* 二十面体

$$n = 1 + \sum_{l=1}^p (10l^2 + 2) : 13, 55, 147, 309, 561 \dots$$

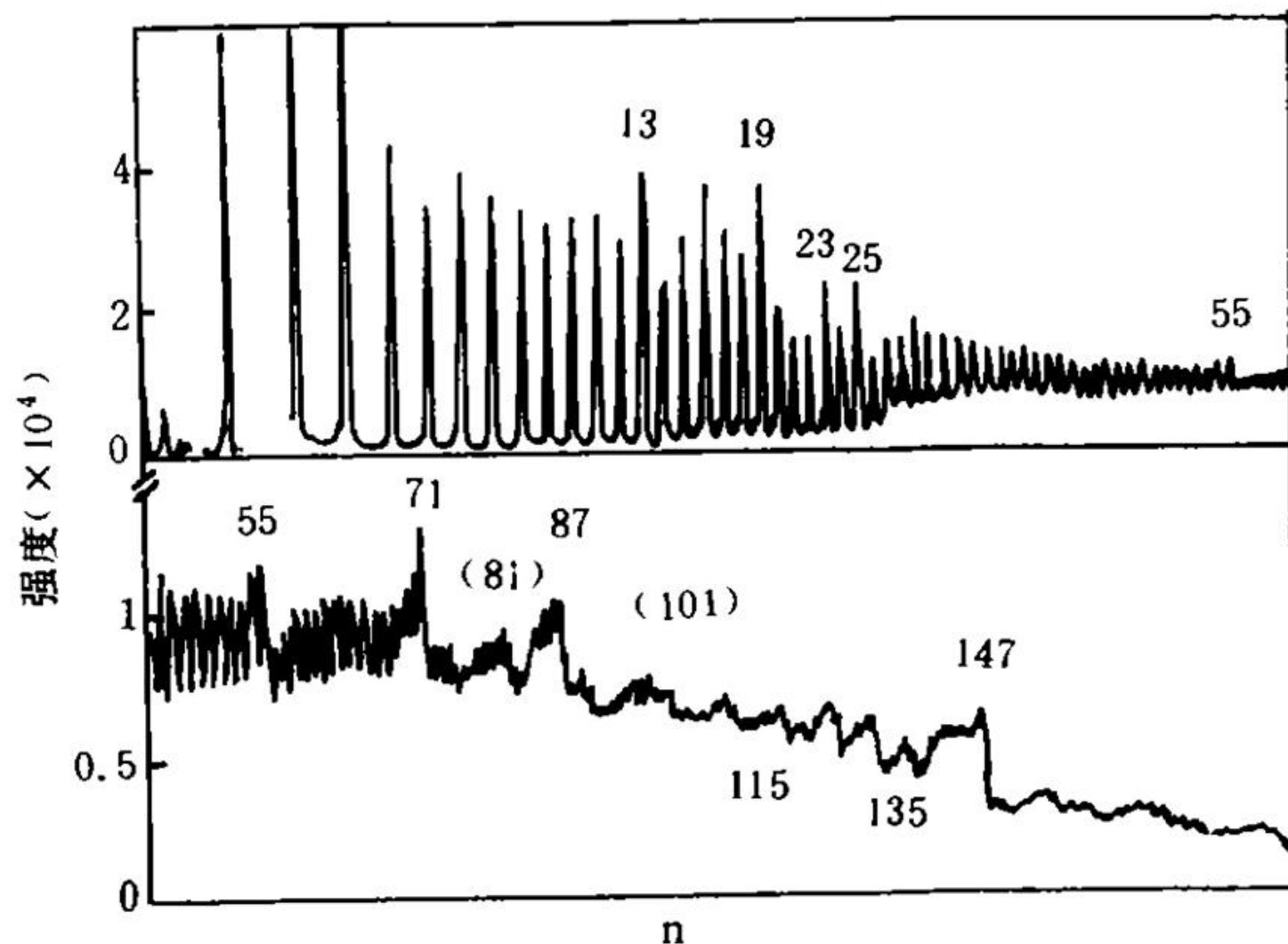


图 5 Xe 团簇的质谱, 所标的数字为幻数所在处,

完整版, 请访问 www.kaoyancas.net 科大科院考研网, 专注于中科大、中科院考研

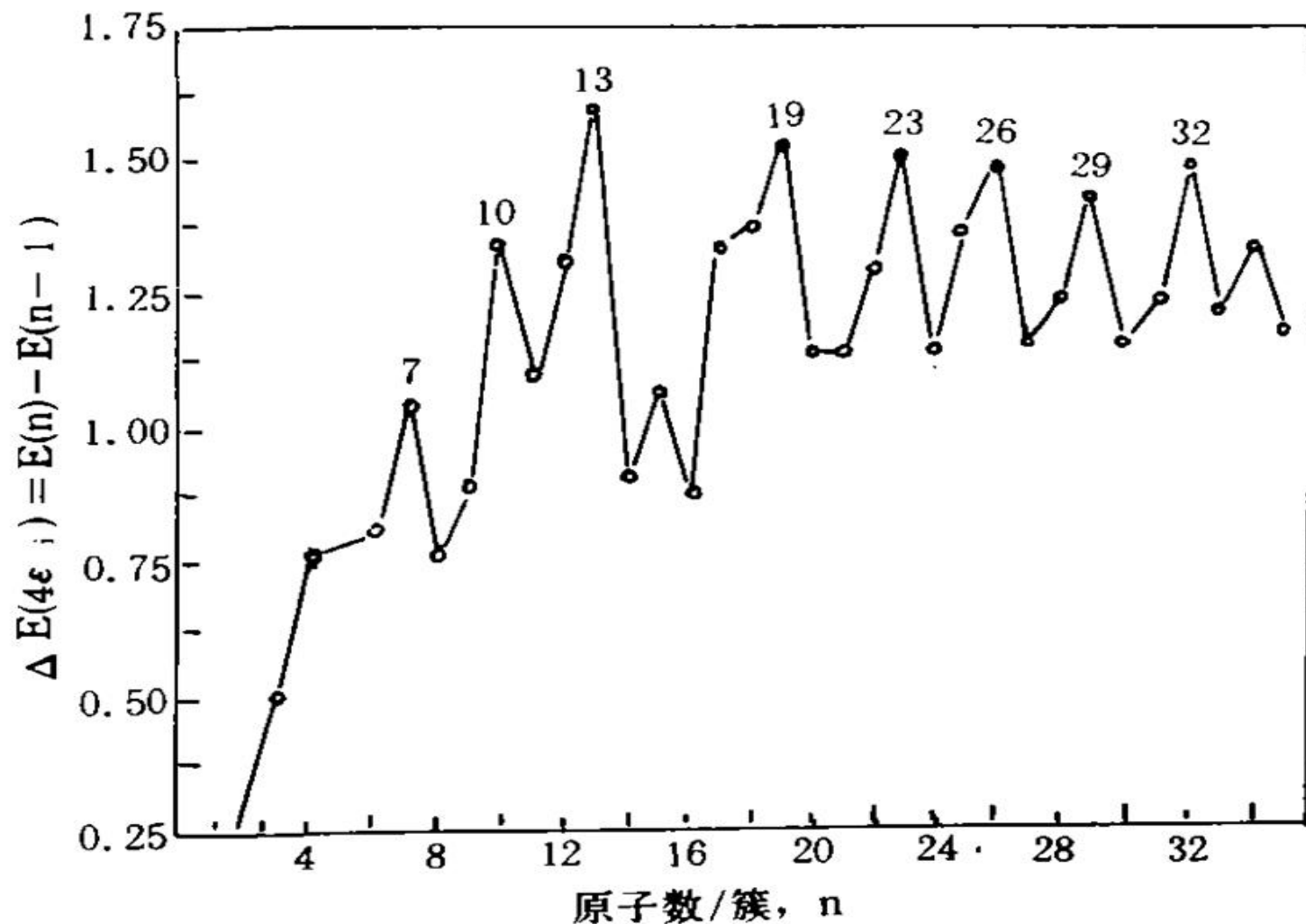


图 6 相邻两团簇之间束缚能之差

$\Delta E(n) = E(n) - E(n-1)$ 随 n 的变

化^[8]

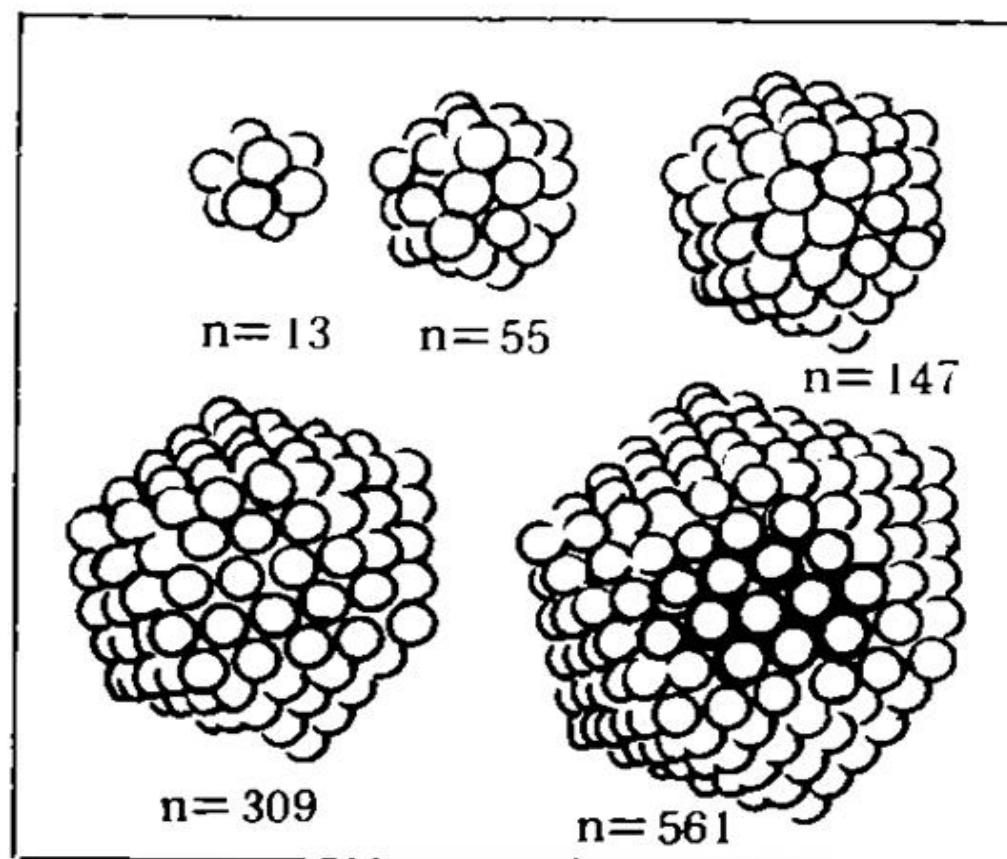


图 7 各种尺寸的
Mackay 二十面体。

(2). 碱金属卤化物团簇

位置序起主导作用 (LiF, NaCl, CuBr, CsI...)

微晶型 ($Li(LiF)_n$)⁺ 络合物分子型 (LiF)_n⁺

碱金属卤化物团簇中离子之间的互作用可以表示为

$$V_{ij} = \frac{Z_i Z_j}{r_{ij}} + A \exp(-r_{ij}/\rho) - \frac{Z_i}{r_i^3} (\mu_j \cdot \mathbf{r}_{ij}) - \frac{Z_j}{r_{ij}} (\mu_i \cdot \mathbf{r}_{ij}) \\ - \frac{3}{r_{ij}^5} (\mu_i \cdot \mathbf{r}_{ij}) (\mu_j \cdot \mathbf{r}_{ij}) - \frac{\mu_i \mu_j}{r_{ij}^3} + \frac{\mu_i^2}{2\alpha_i} + \frac{\mu_j^2}{2\alpha_j}$$

其中第一项表示相距 r_{ij} 两点电荷 Z_i 和 Z_j 之间的库仑作用，第二项是短程 Born-Mayer 排斥作用，第三和第四项给出点电荷 Z_i 和第 j 个原子的偶极距 μ_j 的互作用，第五项和第六项代表偶极-偶极互作用，最后两项是偶极短的自能。团簇的全能量是对 i 和 j 的求和，其中成对相互作用只计算一次。

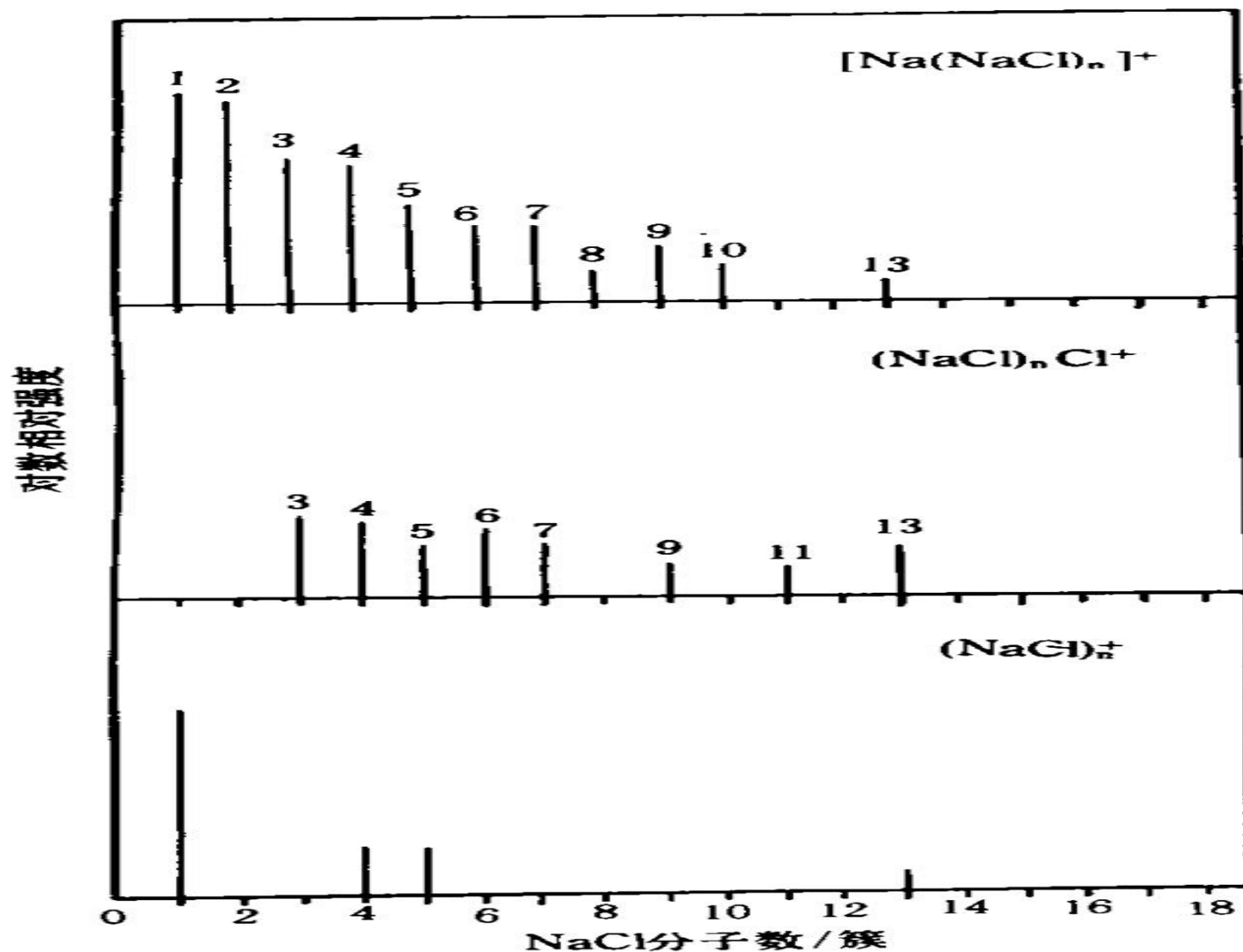


图 9 几种氯化钠离子簇的强度分布
(8keV Ar 轰击 NaCl 晶体)^[15]

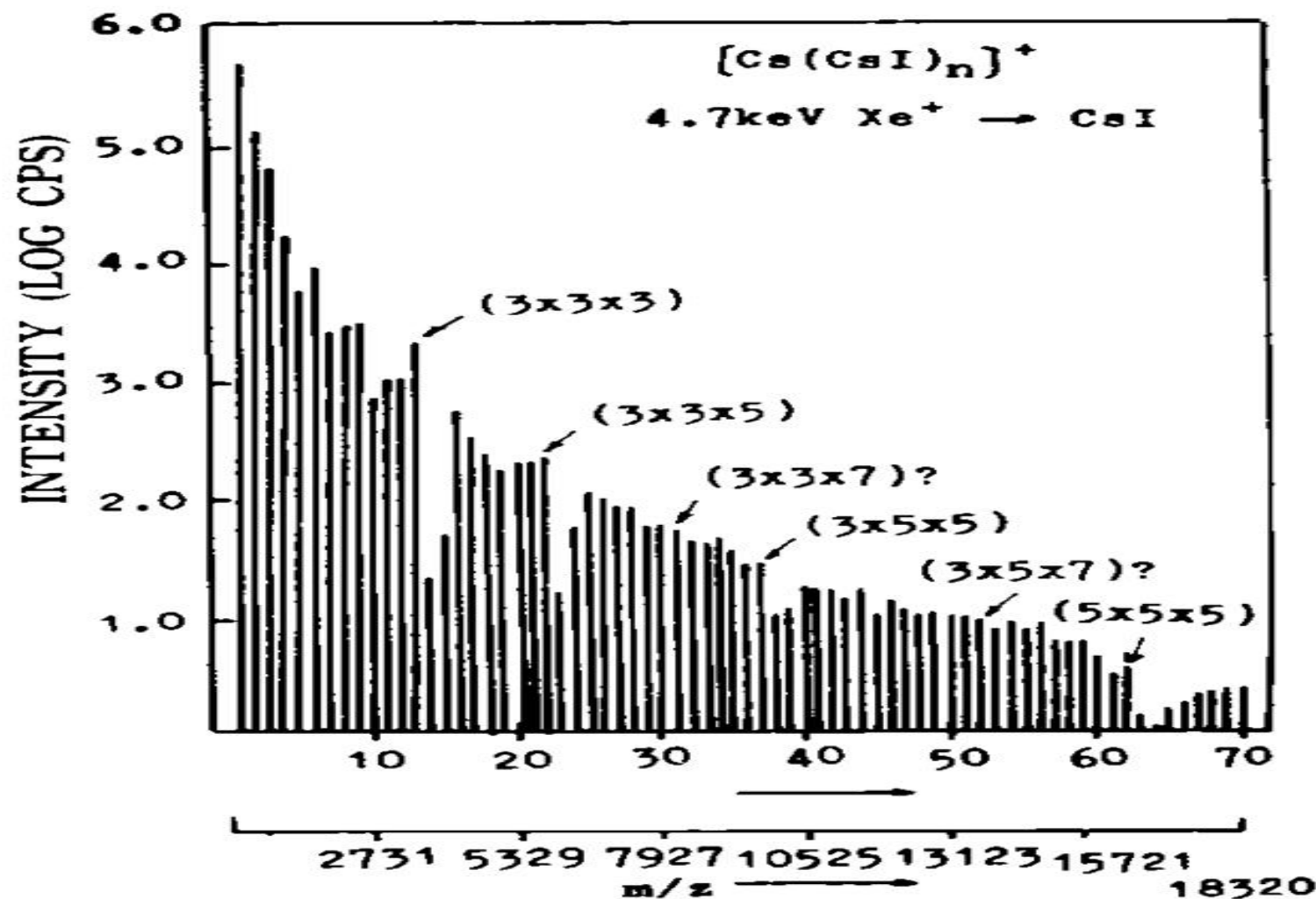
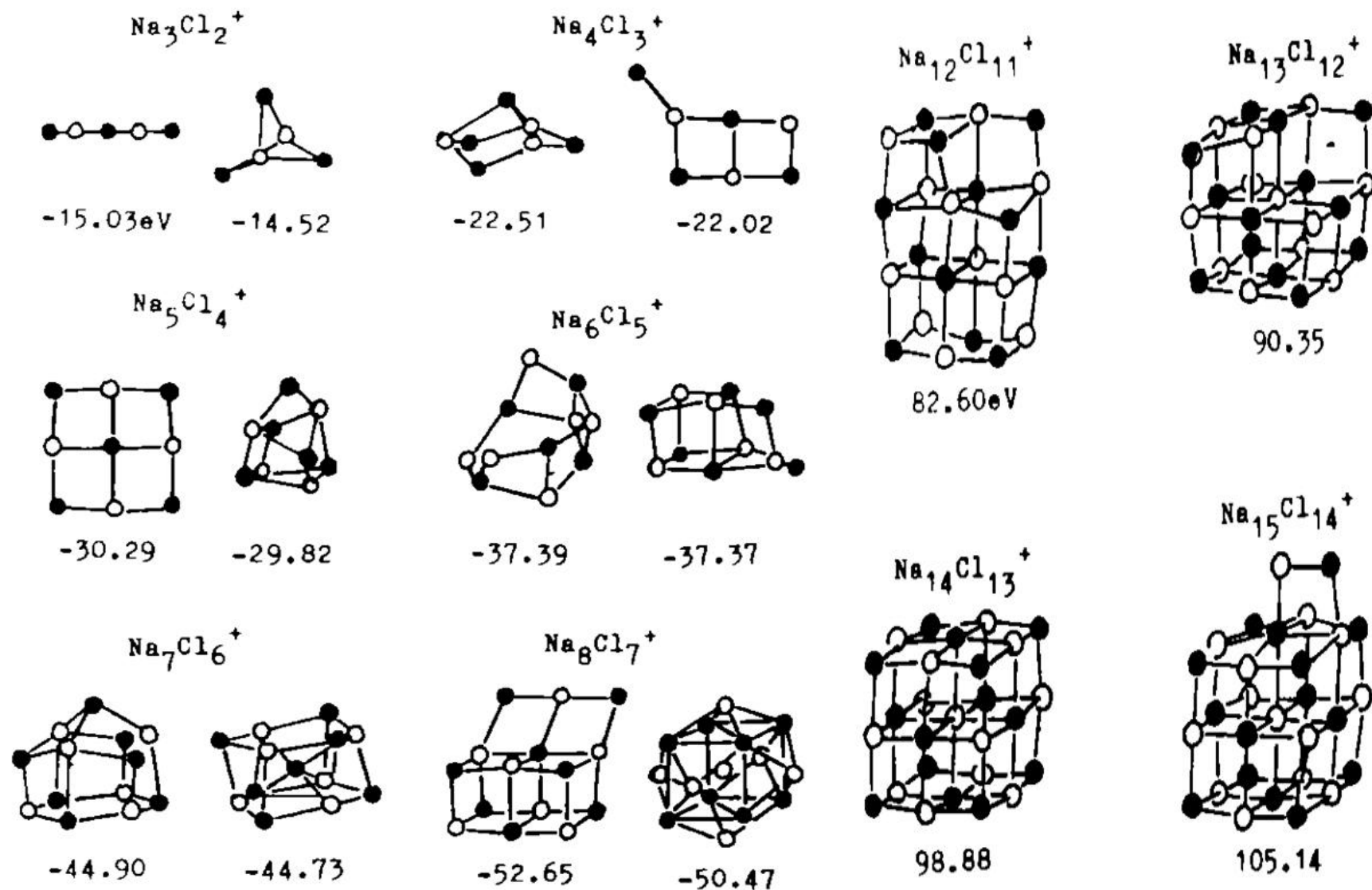
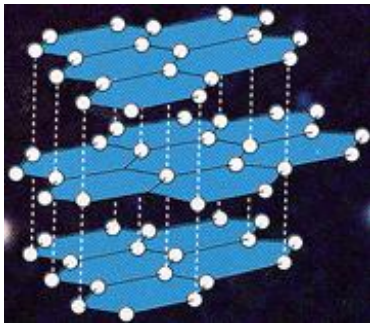


图 10 4.7keV Xe^+ 轰击碘化铯
SIMS 团簇质谱分布

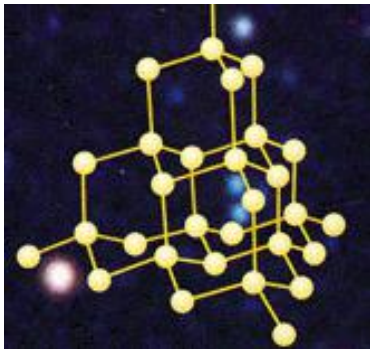


(3). C_{60} 团簇 共价键团簇



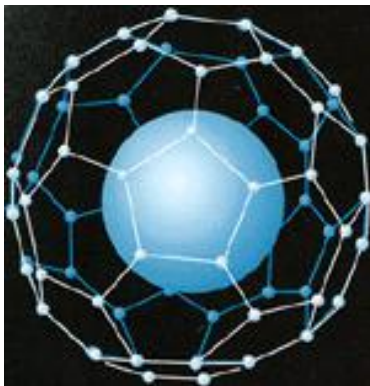
- **Graphite**

- Soft and black and the stable, common, form of carbon.
- Very light and resistant
- Atom is at the corners of fused hexagon in parallel layers.



- **Diamond**

- Hard and transparent and the unusual form of carbon.
- Strong thermal conductivity.
- Atom is bound to four other carbon atoms in a regular repetitive pattern.



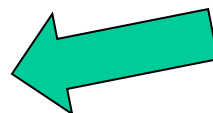
- **C60**

- A third allotropic form of very stable spheres(1985)
- Formed when graphite is evaporated in an inert atmosphere.
- Assumed C60 consists of 12 pentagons and 20 hexagons with carbon atoms at each corner, as a soccer ball.
- Names

An idea from outer space

- The serendipitous discovery

Prof. Curl
Prof. Smalley
had built an apparatus which
could analyze, evaporate
almost any material with a
laser beam

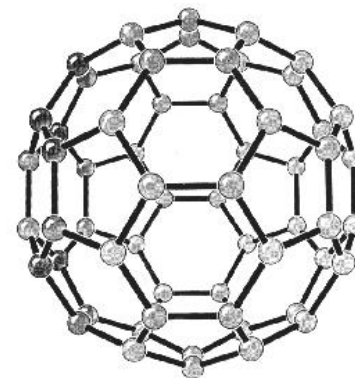
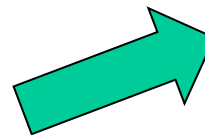


Contact

Prof. Kroto wanted
Long-chained carbon
which could form
red giant stars



Collaboration



C60 (Fall, 1985)

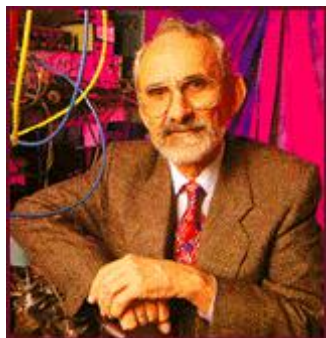
Fullerene Science

- 1985: C₆₀-discovered (Nature **318**, 162)
- 1990: C₆₀-macroscopic scale synthesis (Nature **347**, 354)
- 1991: Carbon nanotubes-discovered(Nature **354**, 56)
- 1996: Noble prize for C₆₀

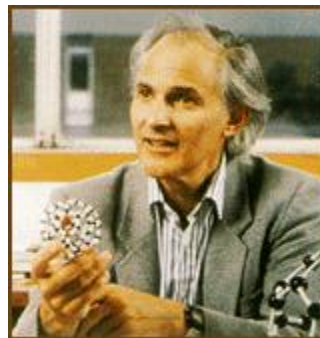


The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"



Prof. Robert F. Curl, Jr
Rice University, Houston
TX, USA

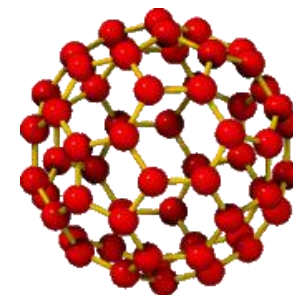


Prof Sir Harold W. Kroto
University of Sussex
Brighton, England



Prof. Richard E. Smalley
Rice University, Houston
TX, USA

Reference : <http://www.nobel.se/chemistry/laureates/1996>



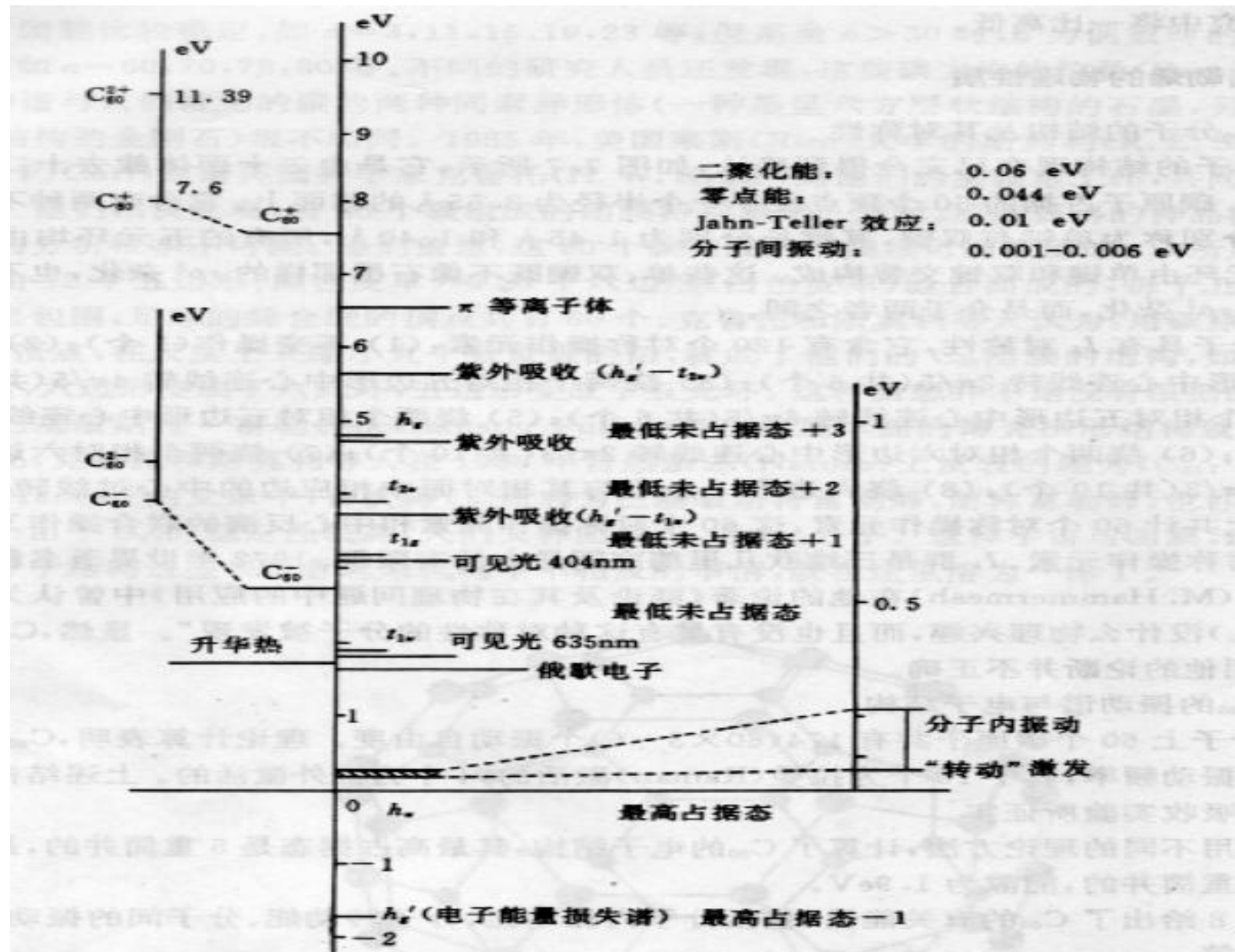
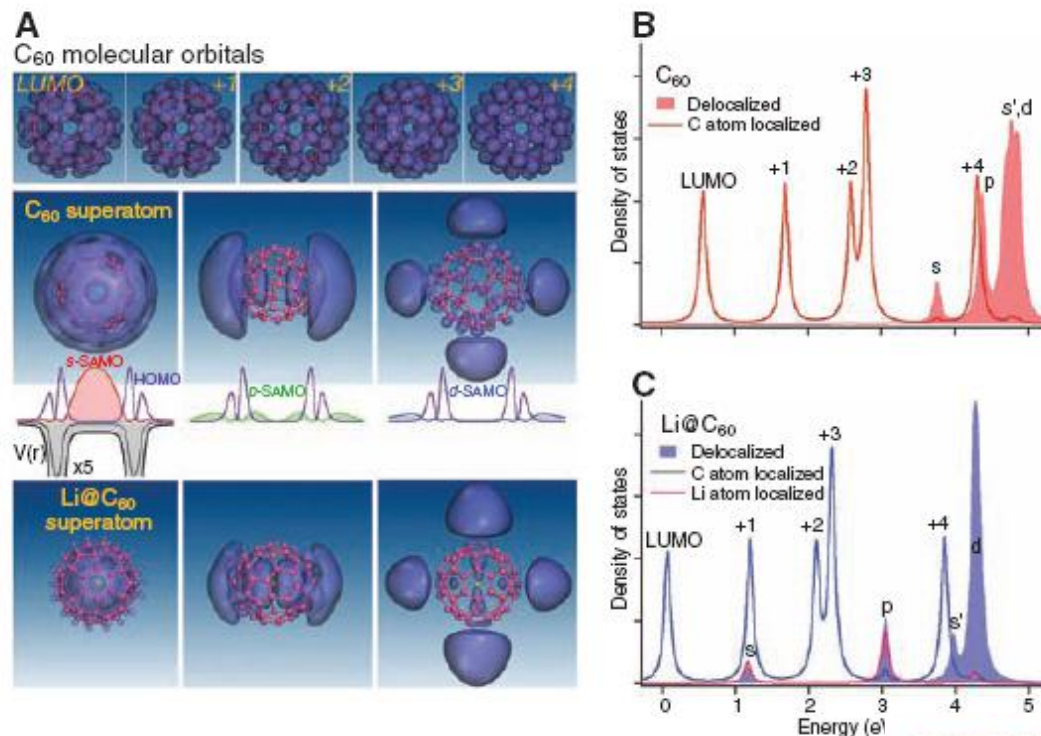


图 7.8 C_{60} 的有关能量参数

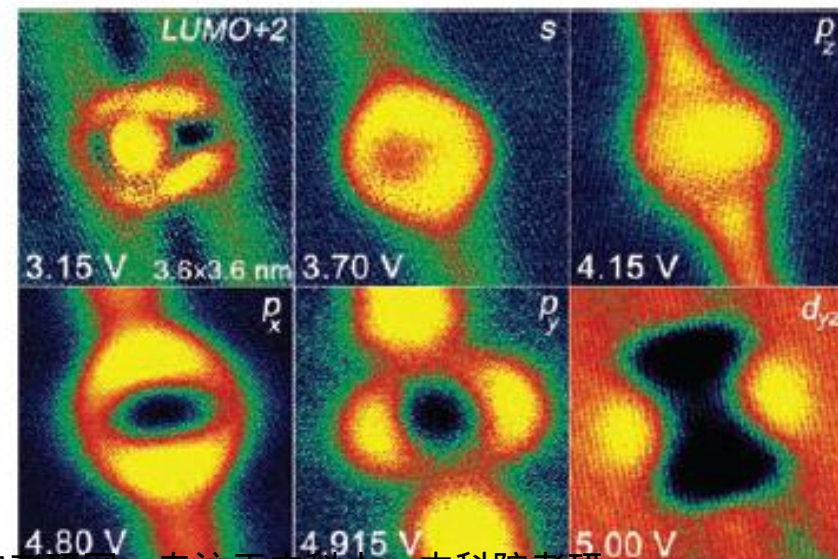


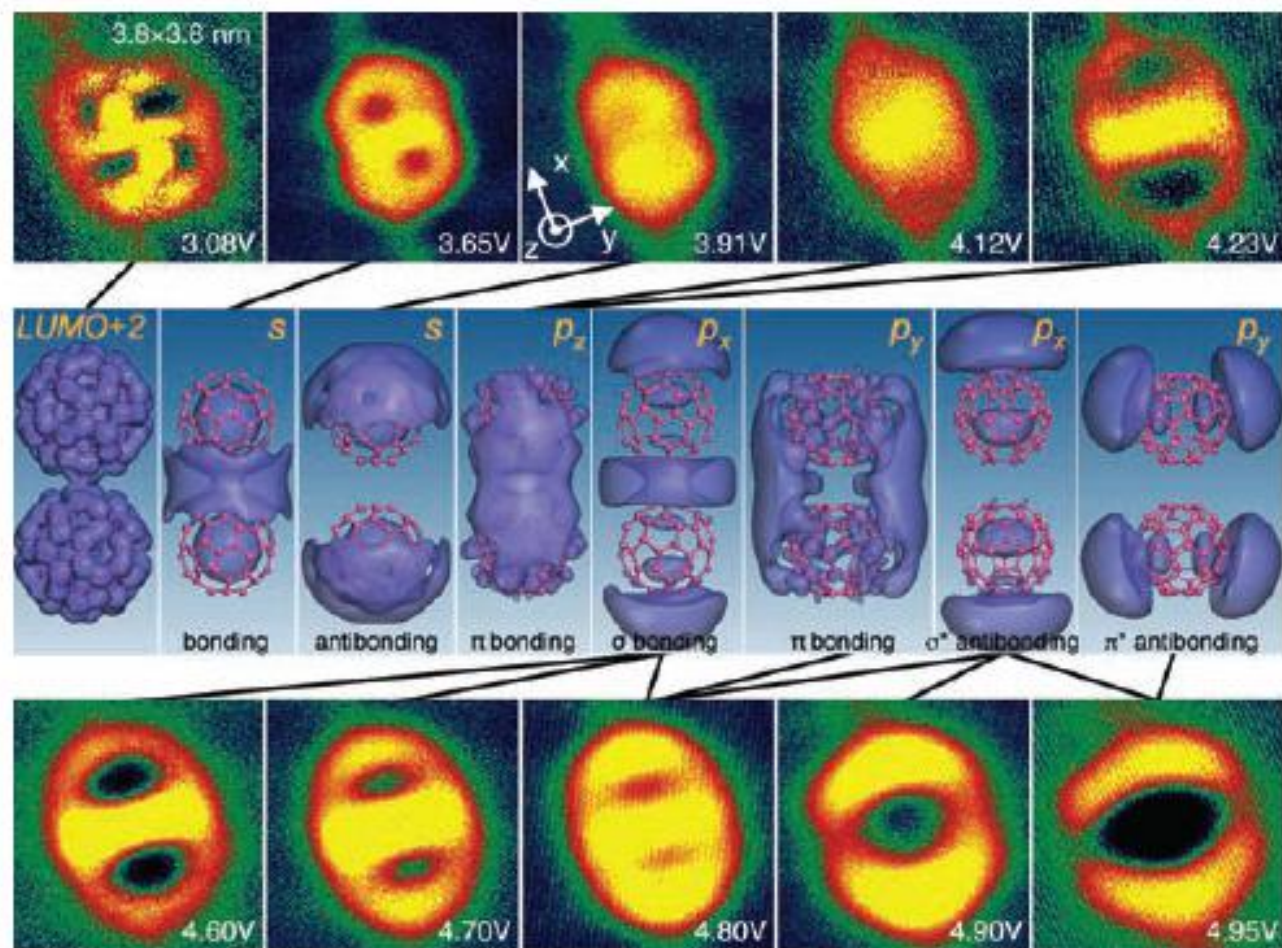
Atomlike, Hollow-Core Bound Molecular Orbitals of C₆₀

Min Feng, *et al.*

Science **320**, 359 (2008);

DOI: 10.1126/science.1155866





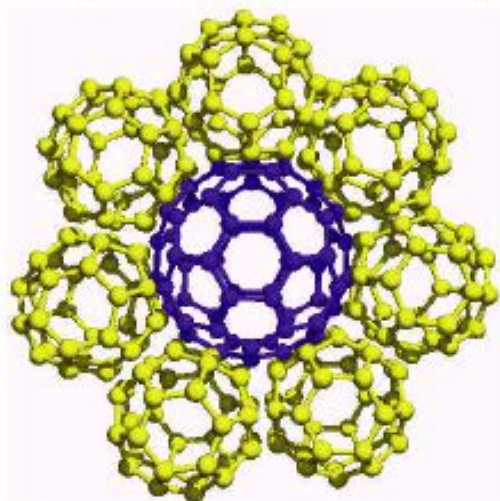


New Fullerene Species, C_{36} , Discovered

C_{36} investigated theoretically
(Cohen, Louie, Côté, Grossman, 1998)

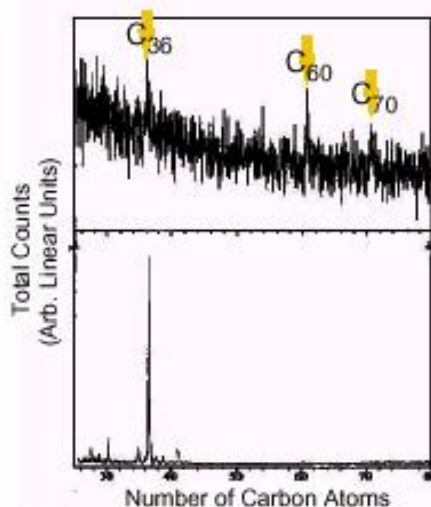
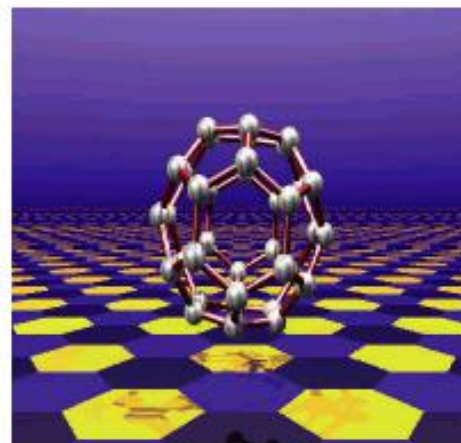


C_{36} synthesized in bulk quantities
(Piskoti, Zettl—1998)



C_{36} molecules (yellow) have higher curvature than C_{60} (blue) resulting in high reactivity and large electron-phonon coupling.

A highly strained sp^2 -bonded C_{36} cage molecule (diameter $\sim 5\text{\AA}$) is shown above a stylized hexagonal graphite surface which represents the lowest energy form of carbon.

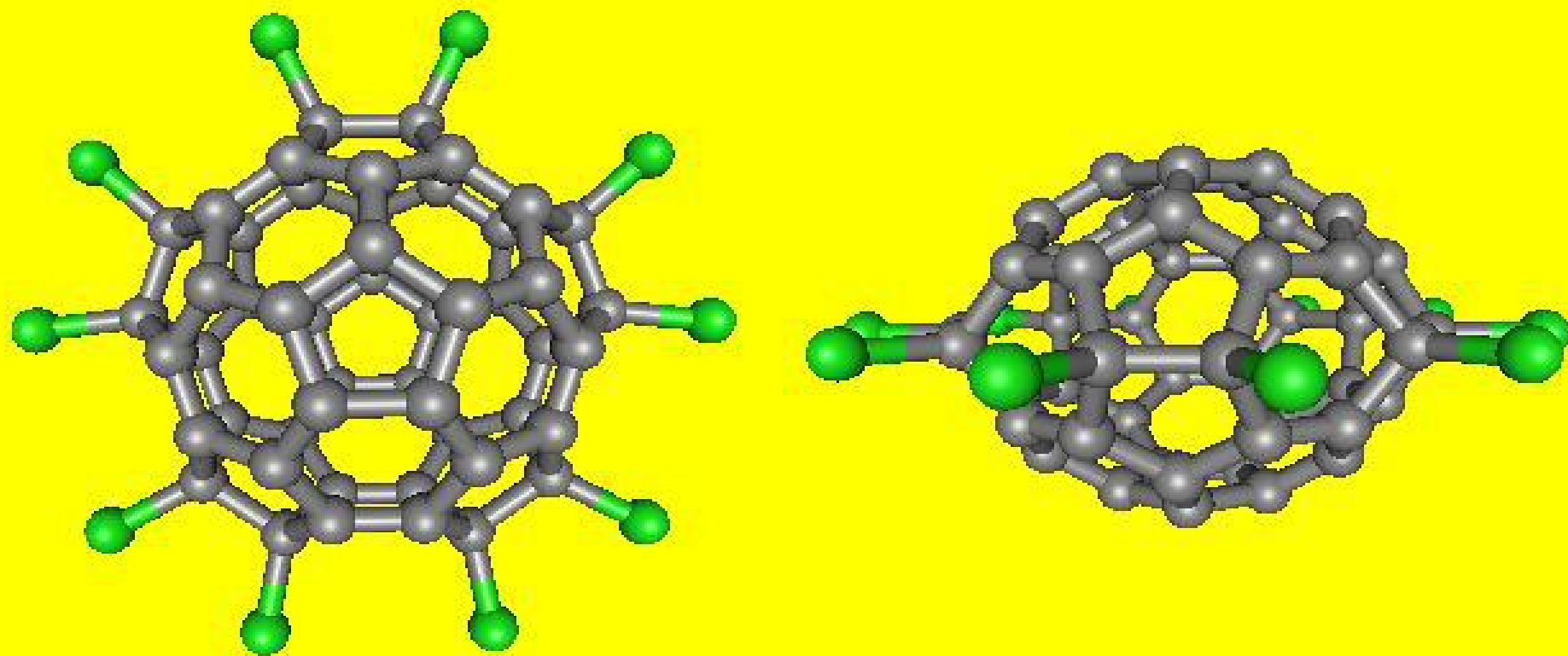


C_{36} synthesis and purification shown in mass spectrum of crude (top) and isolated material (bottom).

Alex Zettl, Charles Piskoti
Materials Sciences Division
Berkeley Lab

98-8

$C_{50}Cl_{10}$ 的立体结构模拟图



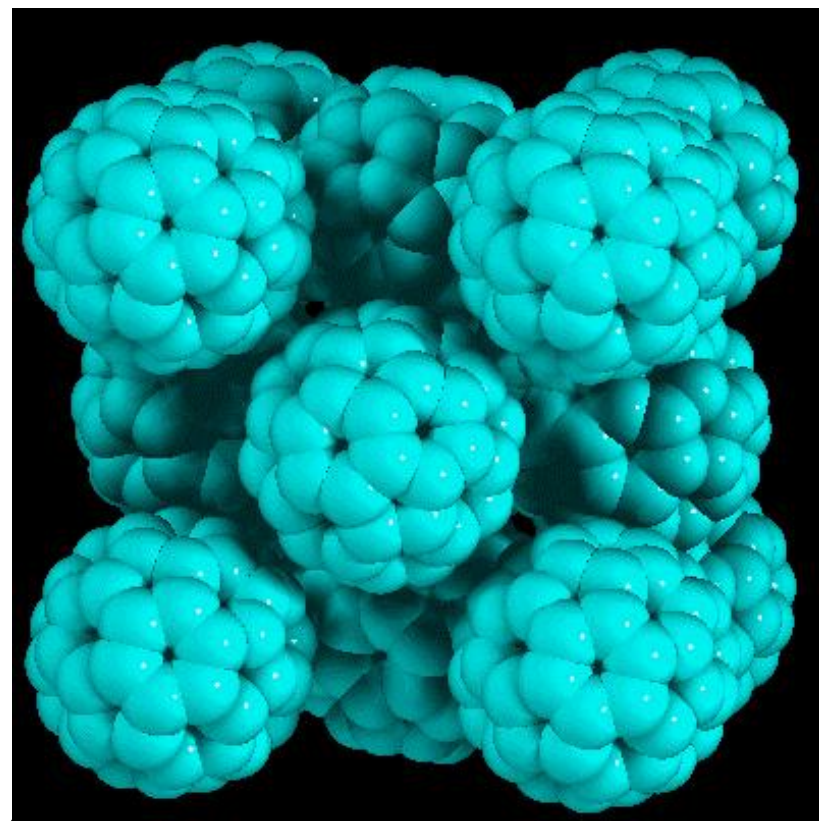
Usefulness of hollow sphere structure

((1))Filter

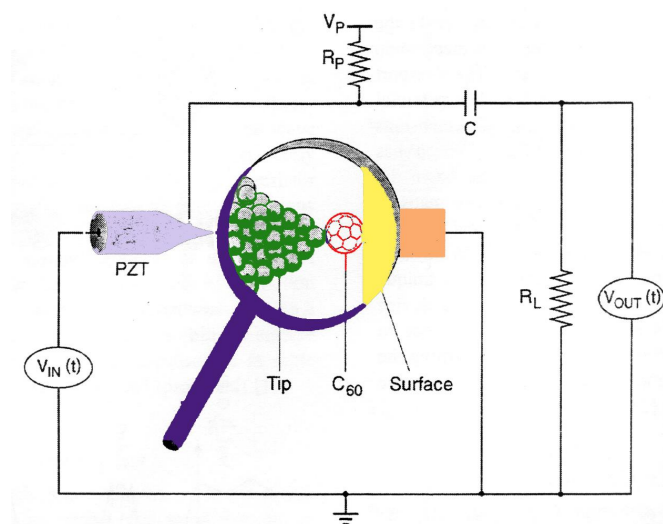
((2))Superconductivity

((3))Building material of objects

((4))Expansion to nanotube



Fullerene-based single molecule devices

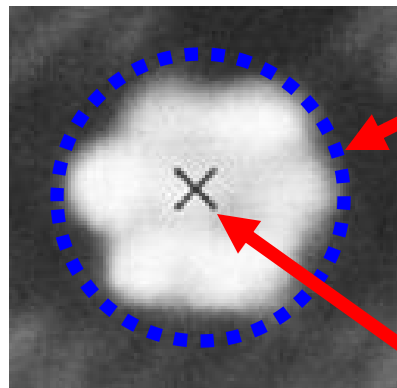


Contents

- **Switch and Transistor**
- **Rectifier**
- **Magnetoresistance**
- **Oscillator**
- **NDR**
- **Conduction and Others**

Switch

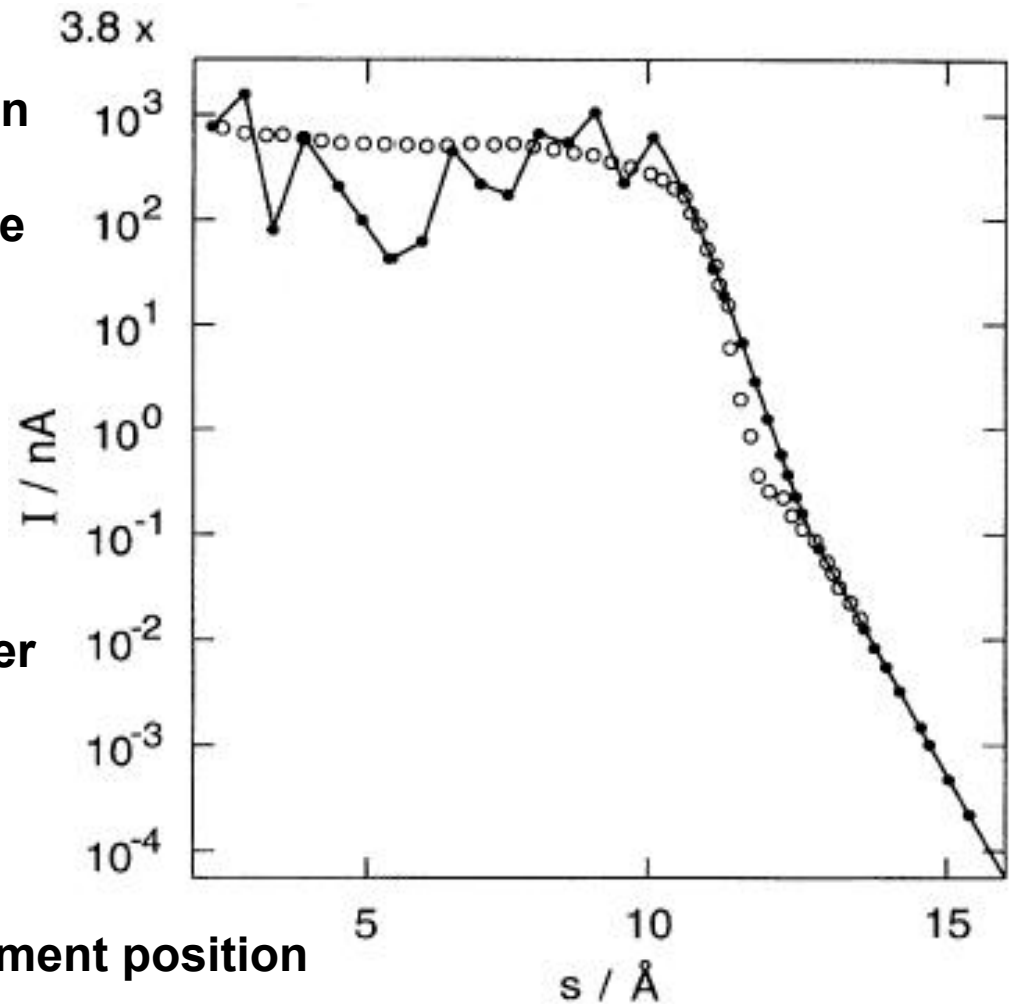
- Tunneling region to contact region
- Deformation of C_{60} contributes the increase of current
- Electrical resistance is $54.80 \text{ M } \Omega$



$C_{60}/\text{Au}(110)\text{-}1\times 2$

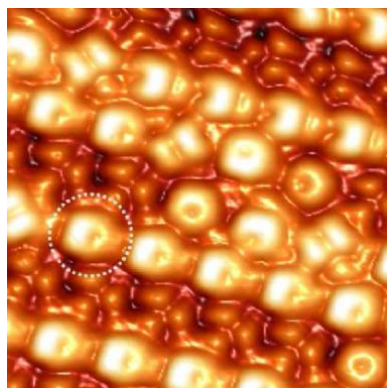
C_{60} cluster

measurement position

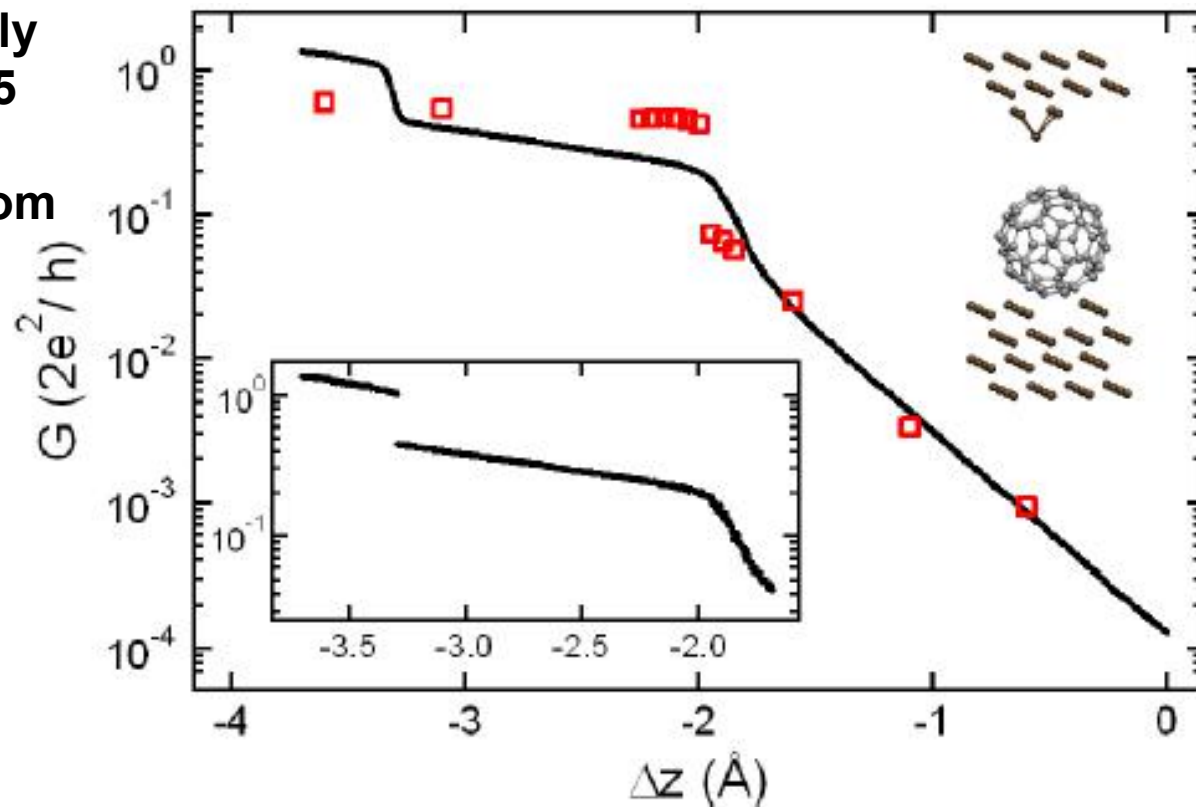


Current I as a function of tip displacement s at 300K

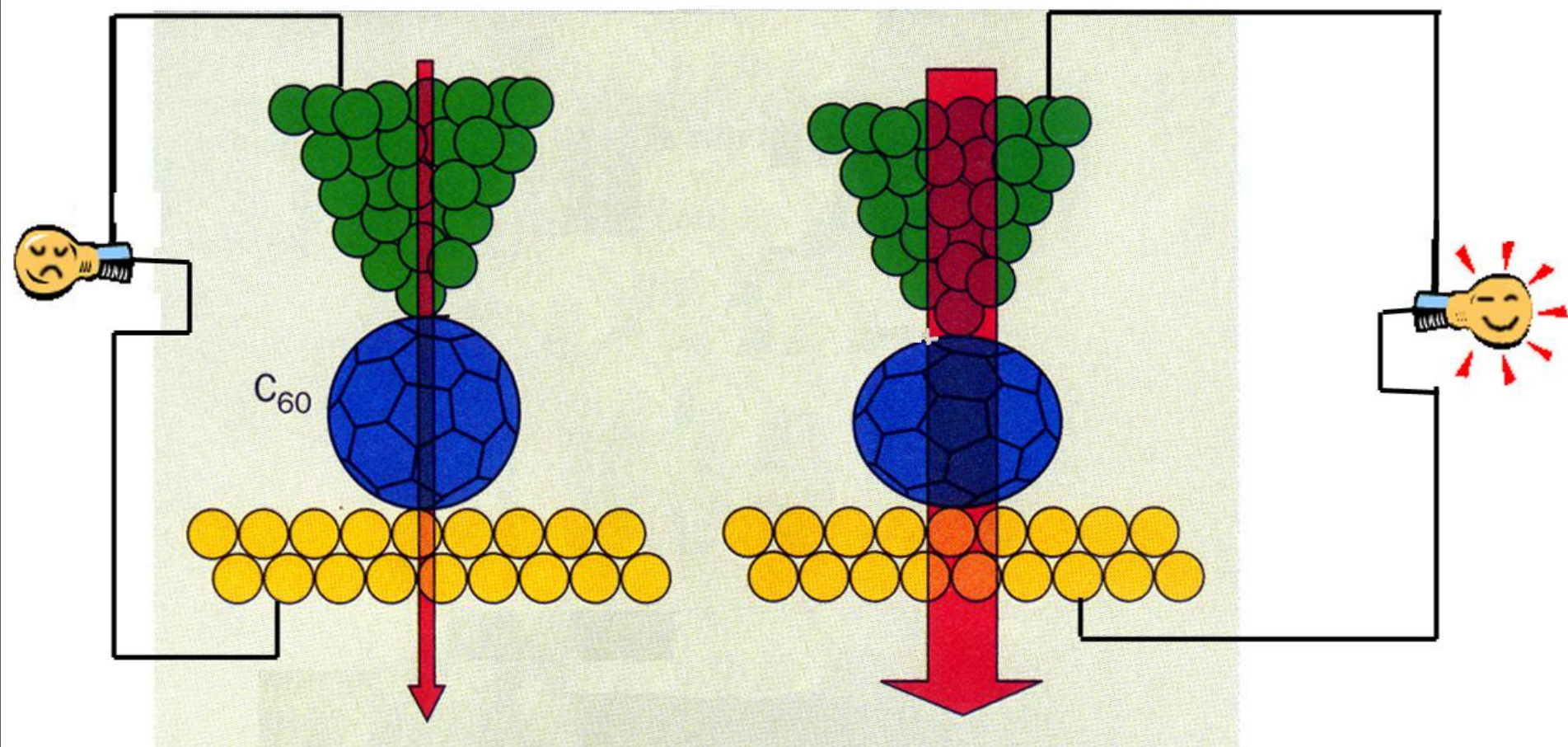
The conductance rapidly increases to about 0.25 conductance quanta in the transition region from tunneling to contact.



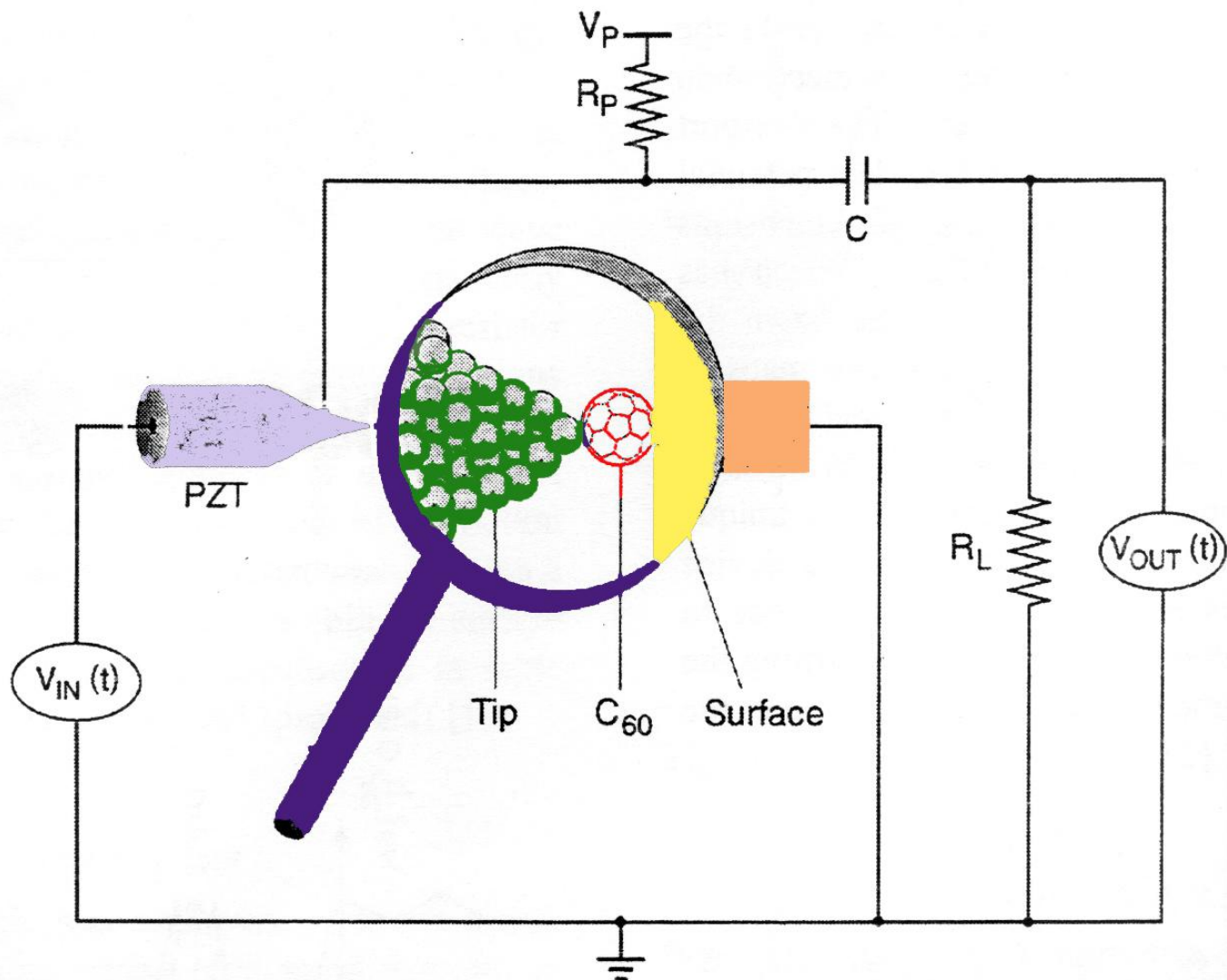
$C_{60}/Cu(100)$



Conductance vs tip displacement at 8K



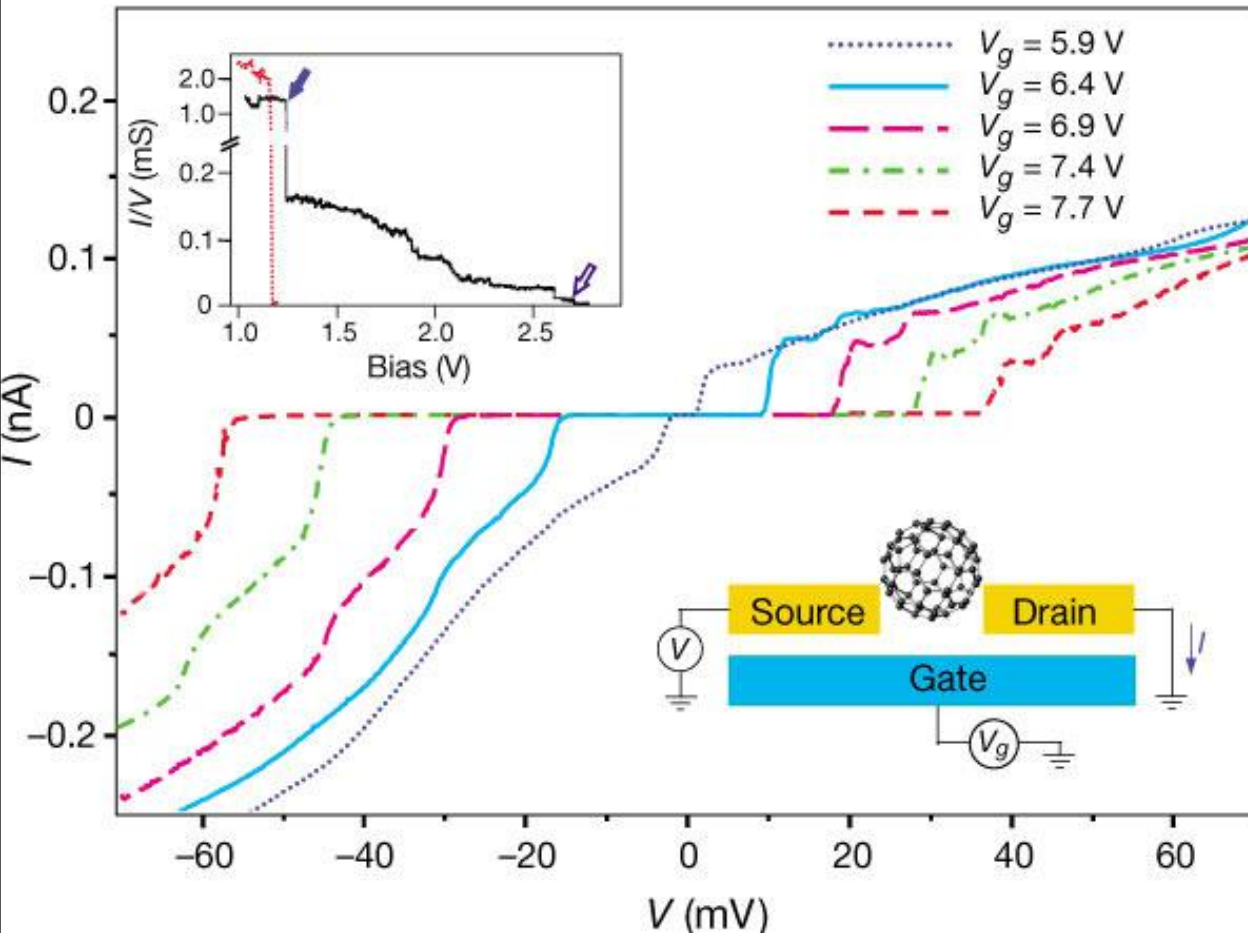
Single-molecule on-off



Single-molecule electromechanical amplifier

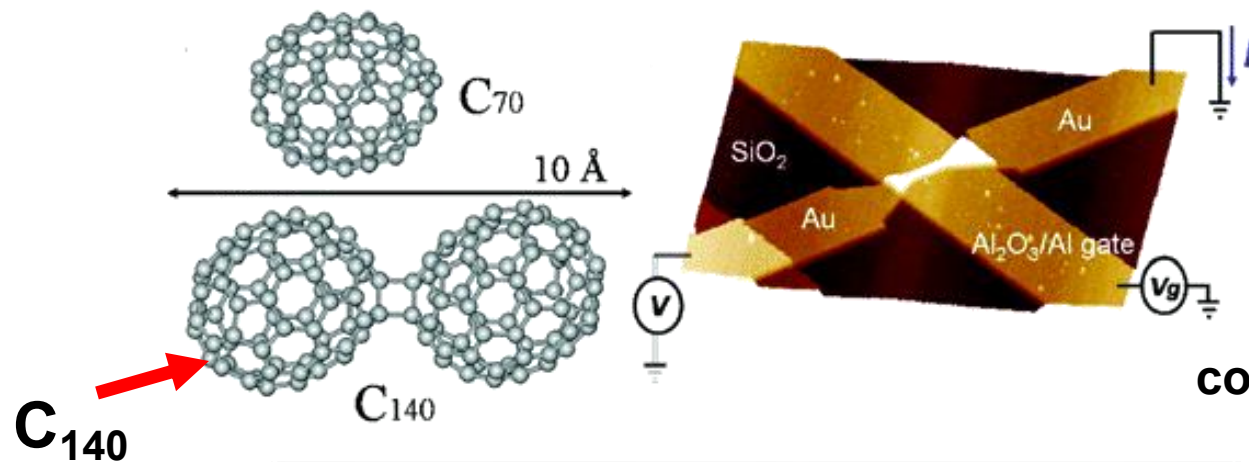
Transistor

Au-C₆₀-Au system

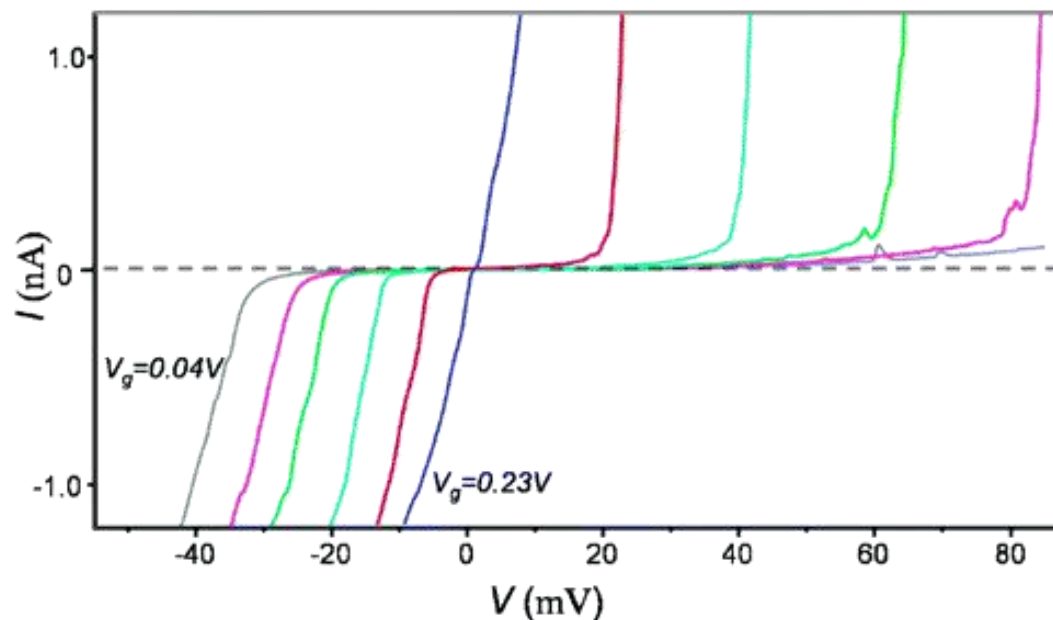


- **Strongly suppressed conductance near zero bias voltage followed by step-like current jumps at higher voltages**
- **The current through the transistor and the voltage width of the zero conductance region can be changed by changing V_g reversibly.**

Current–Voltage (I – V) curves obtained from a single-C₆₀ transistor at $T = 1.5$ K

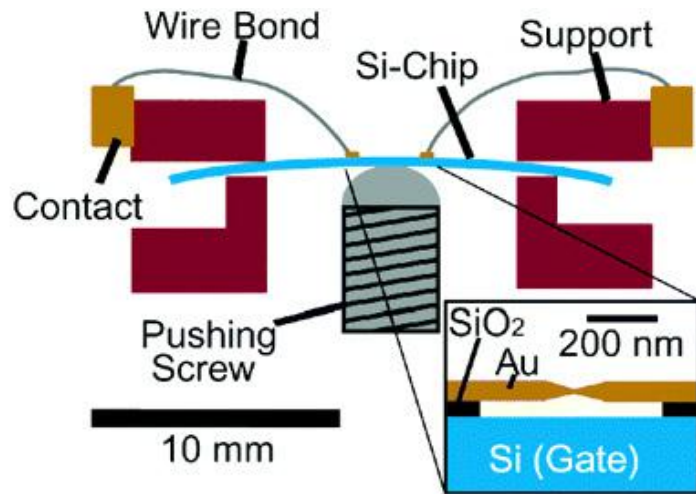


AFM image of continuous Au electrode

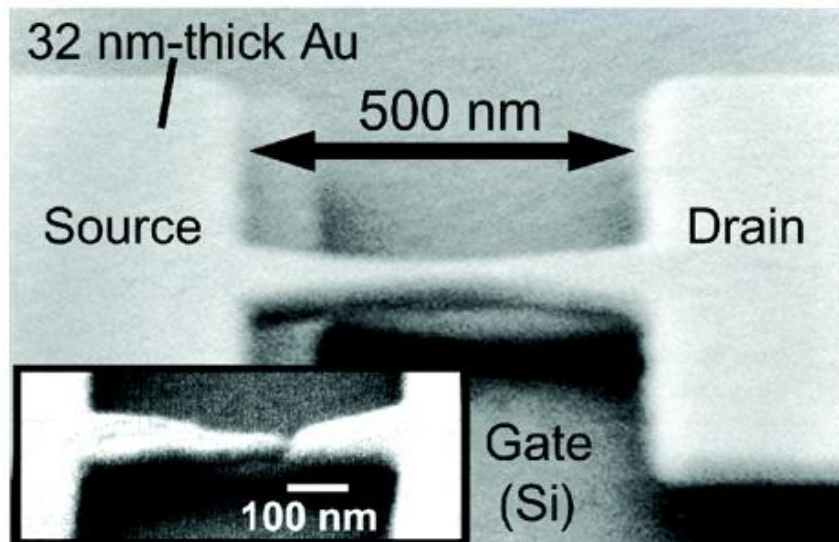


I-V curves from a C_{140} single electron transistor for equally spaced V_g

Au- C_{140} -Au system



A device geometry for single-molecule electronics experiments that **combines** both the **ability to adjust the spacing** between the electrodes mechanically and the **ability to shift the energy levels** in the molecule using a gate electrode



Au-C₆₀-Au system

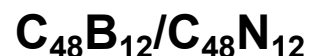
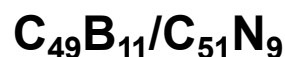
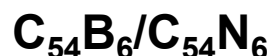
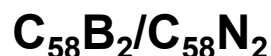
Design of the experimental apparatus and STM image of a MCBJ sample with a silicon substrate gate, before breaking the gold bridge

Rectifier

Double C60

Requirement: The LUMO of the acceptor should lie at or above the Fermi level of the electrode and above the HOMO of the donor

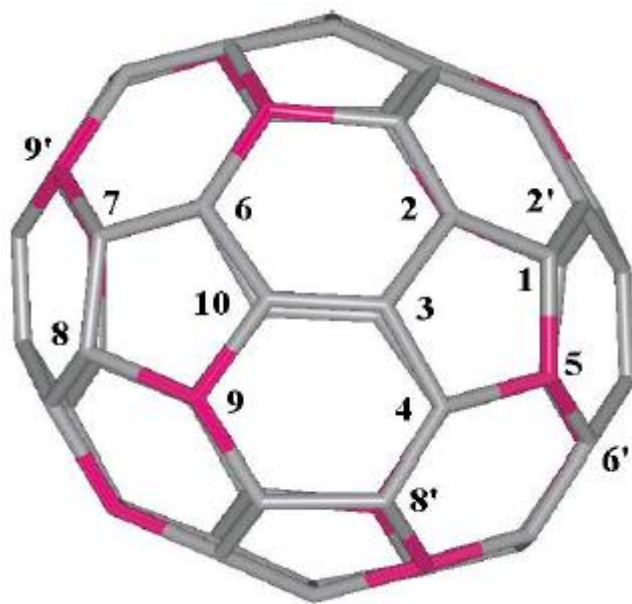
Acceptor/donor pairs



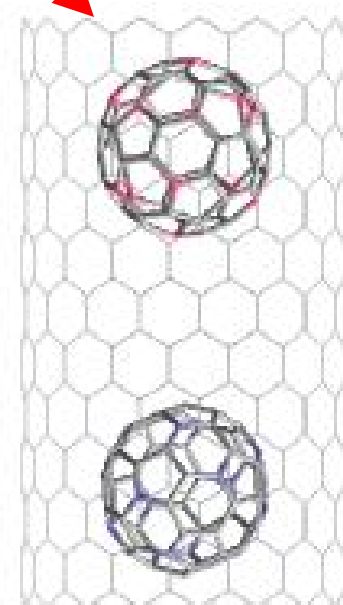
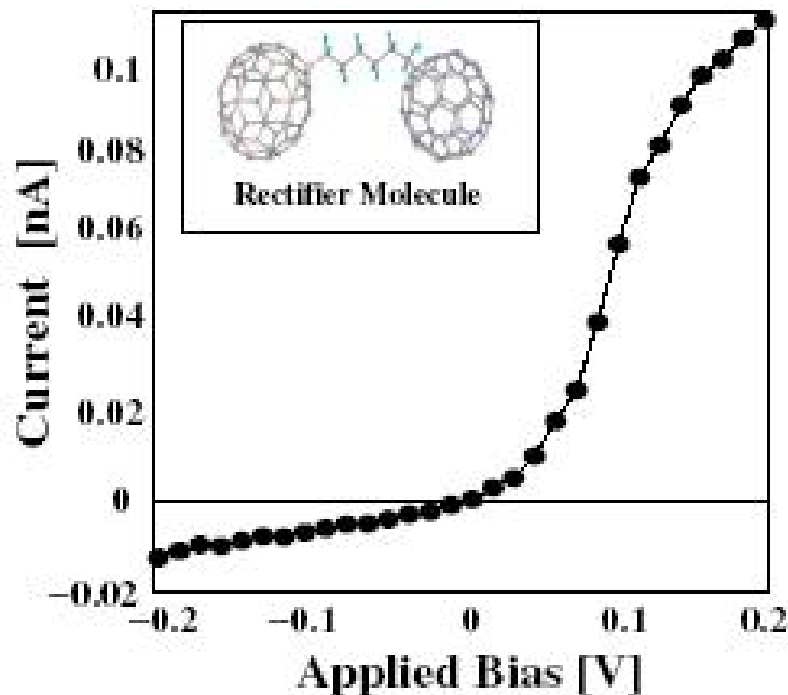
n	$\text{C}_{60-n}\text{B}_n$		$\text{C}_{60-n}\text{N}_n$	
	E_l	E_h	E_l	E_h
1	-4.26	-5.57	-3.63	-4.72
2	-4.64	-5.25	-3.71	-4.64
3	-4.21	-5.49	-3.72	-4.69
4	-4.43	-5.60	-3.91	-4.56
5	-4.59	-5.54	-3.74	-4.56
6	-4.55	-5.49	-3.74	-4.61
7	-4.49	-5.54	-3.58	-4.59
8	-4.62	-5.34	-3.60	-4.41
9	-4.65	-5.43	-3.49	-4.45
10	-4.57	-5.44	-3.31	-4.28
11	-4.45	-5.61	-3.36	-4.35
12	-4.24	-5.58	-2.61	-4.38

The energy (eV) of LUMO (E_l) and HOMO (E_h) calculated for $\text{C}_{60-n}\text{X}_n$ ($\text{X}=\text{B};\text{N}$) using B3LYP/6-31G(d)

A prototype for $C_{48}X_{12}@ (17,0)$ SWNT-based ($X=B;N$) p - n junction



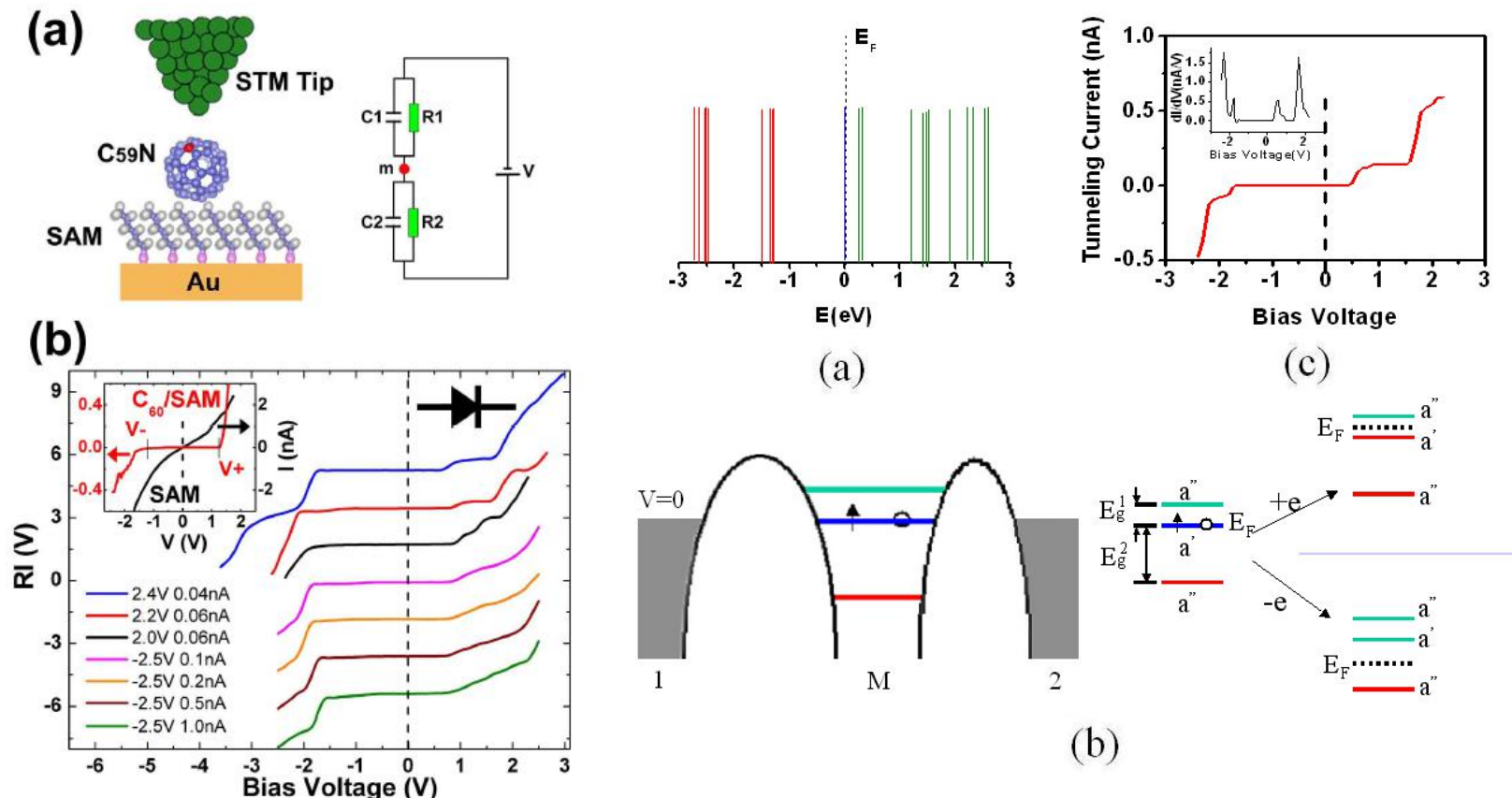
$C_{48}B_{12}$ structure optimized
with B3LYP/6-31G(d)



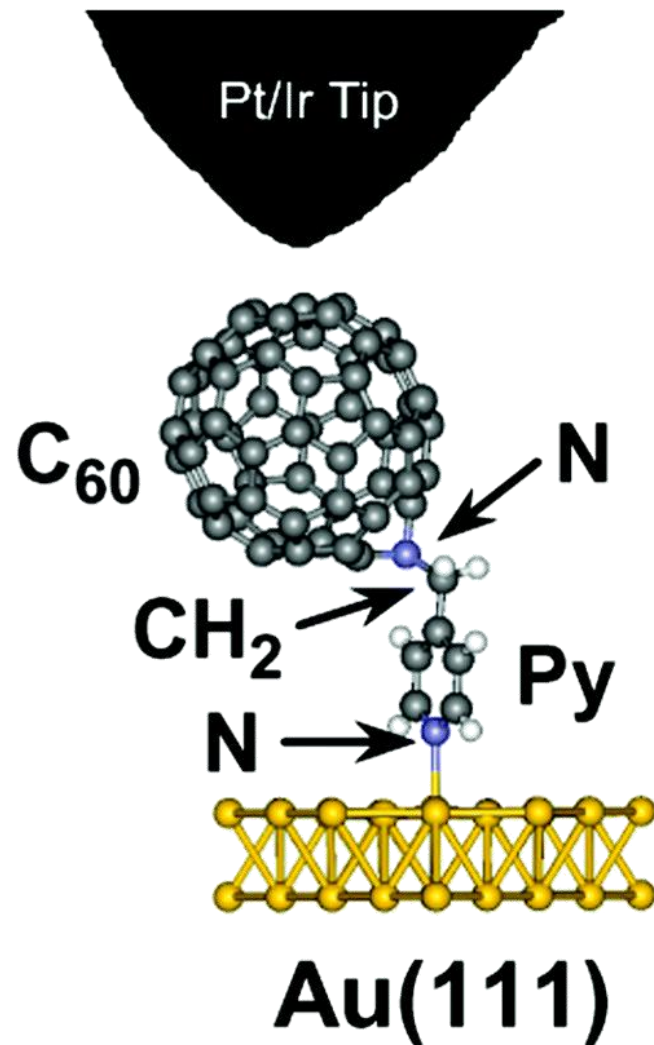
Calculated current through a rectifier $C_{48}B_{12}/C_{48}N_{12}$ pair

Single C59N Molecule as a Molecular Rectifier

J.Zhao *et al.*, Phys.Rev.Lett.,95,045502(2005)

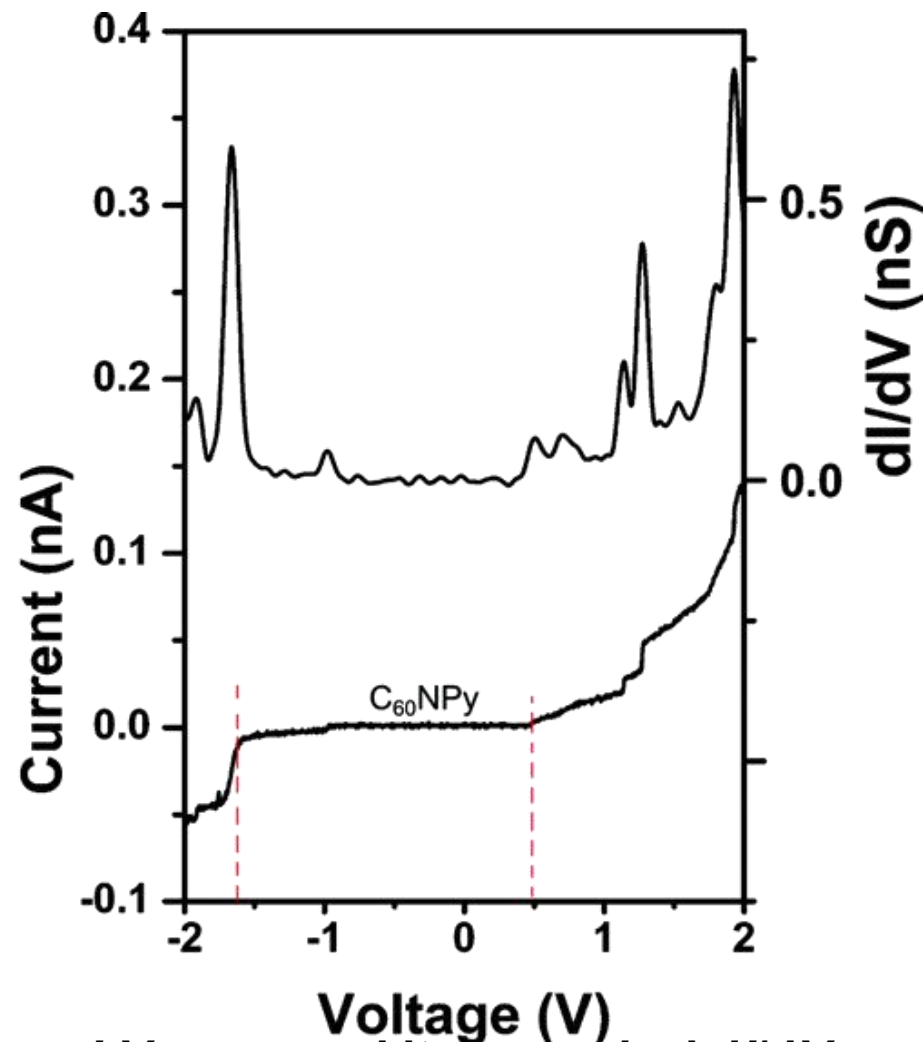


SET+C59N → Molecular rectifier



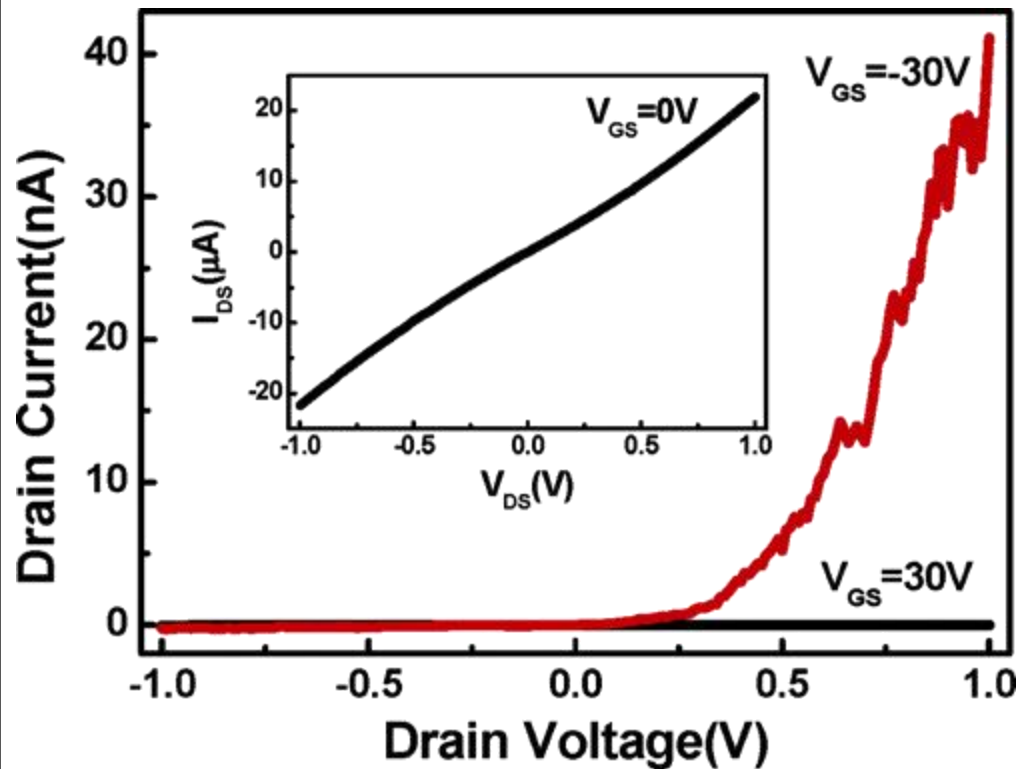
Schematic drawing of the model of the $C_{60}NPy$ on Au(111) surface

Rectifying effect based on the donor-barrier-acceptor (D- ϕ -A) architecture

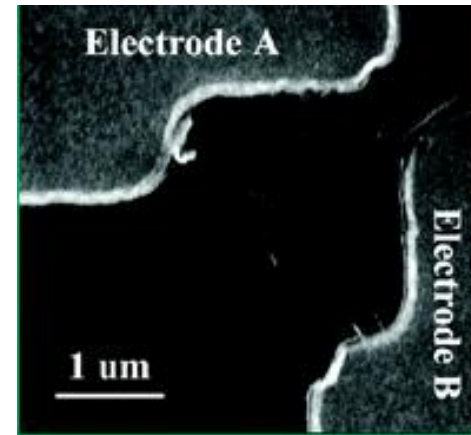


I-V curve and its numerical dI/dV spectrum for $C_{60}NPy$ measured at 5 K taken at a gap voltage of 2.0 V

Gate-controlled rectifying behavior



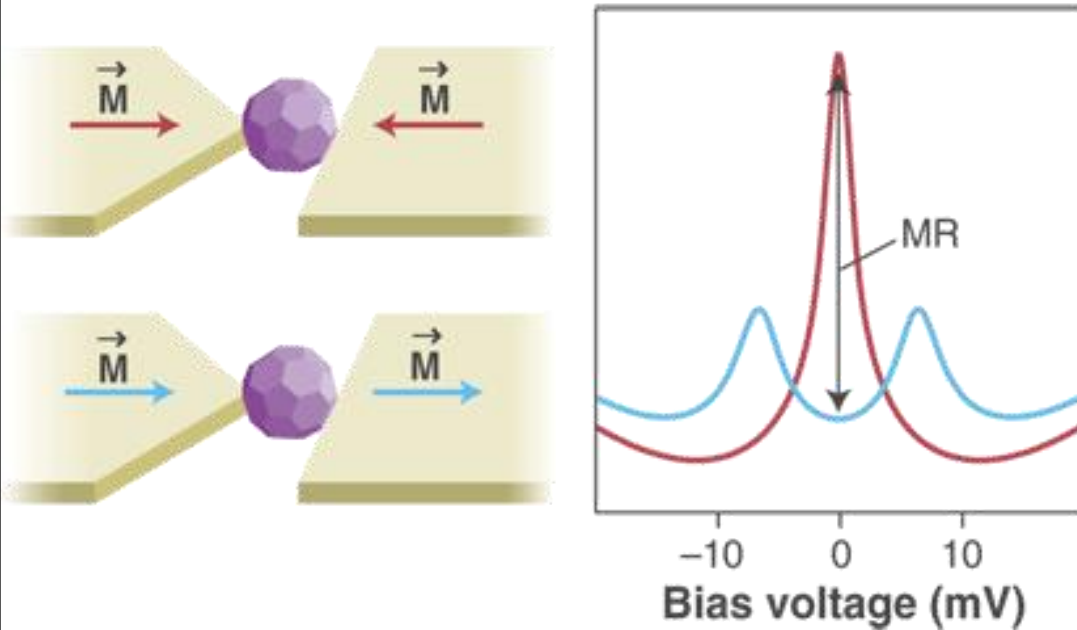
- $C_{70}@SWNT$ networks
- Gate-controlled rectification behavior at room temperature in air
- The current rectification results from highly asymmetric Schottky barriers between semiconducting peapods and the S/D electrodes



Gate-controlled rectifying I_{DS} - V_{DS} characteristics **after electrical breakdown**. Inset: almost linear I_{DS} - V_{DS} curve for pristine device.

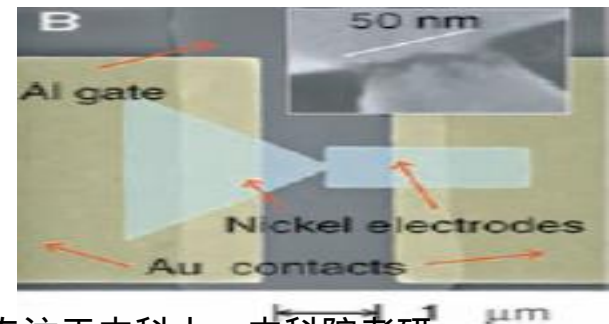
Magnetoresistance

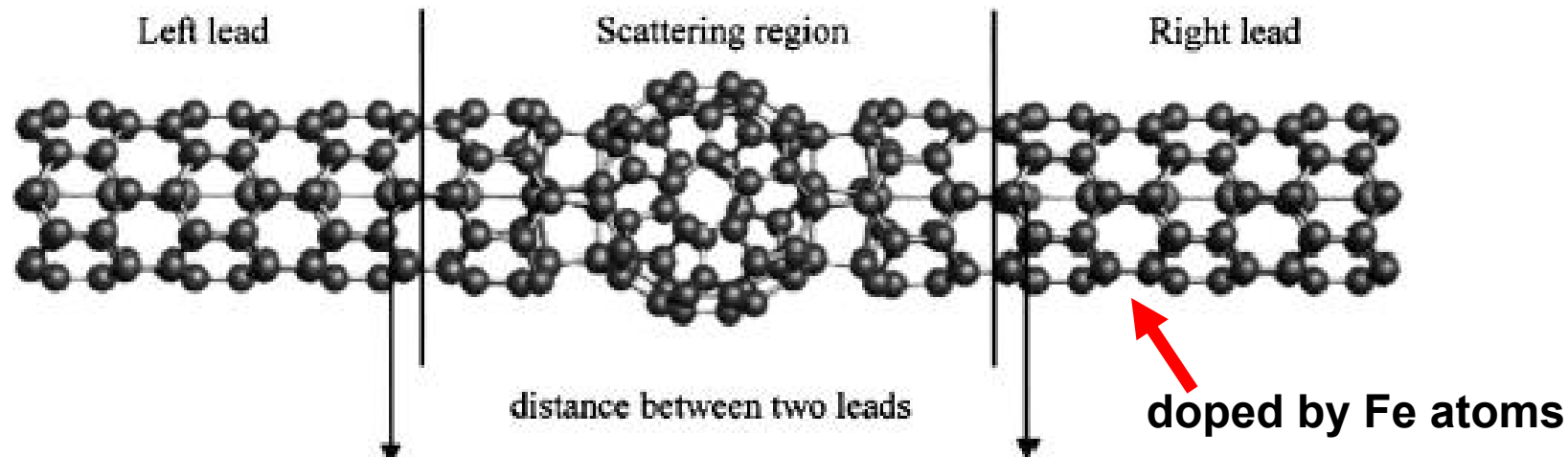
Ni-C₆₀-Ni system (experiment)



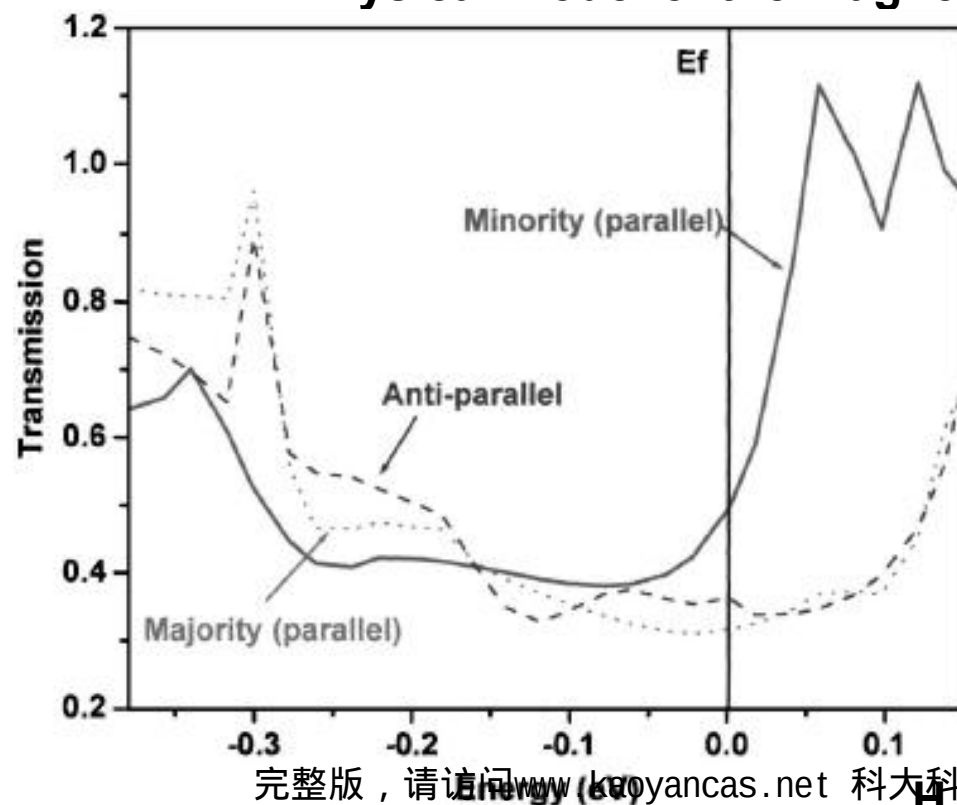
(Left) Artist's view of the C₆₀ quantum dot between ferromagnetic nickel electrodes.
(Right) Differential conductance versus bias voltage of the device for the parallel (blue) and antiparallel state (red).

- For parallel alignment, the Kondo resonance is split by the exchange fields of the two electrodes.
- For antiparallel alignment, the exchange fields of the two electrodes cancel each other, and Kondo resonance is restored at zero-bias voltage.
- This leads to a large magnetoresistance MR, which exceeds the usual tunneling magnetoresistance





Physical model of the magnetic CNT/C₆₀/CNT junction

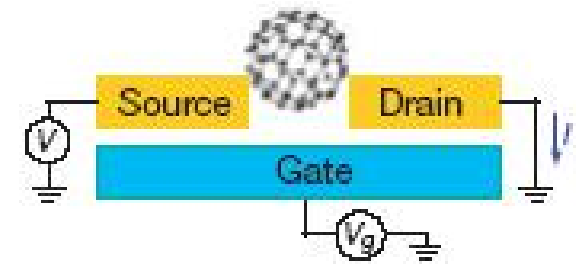
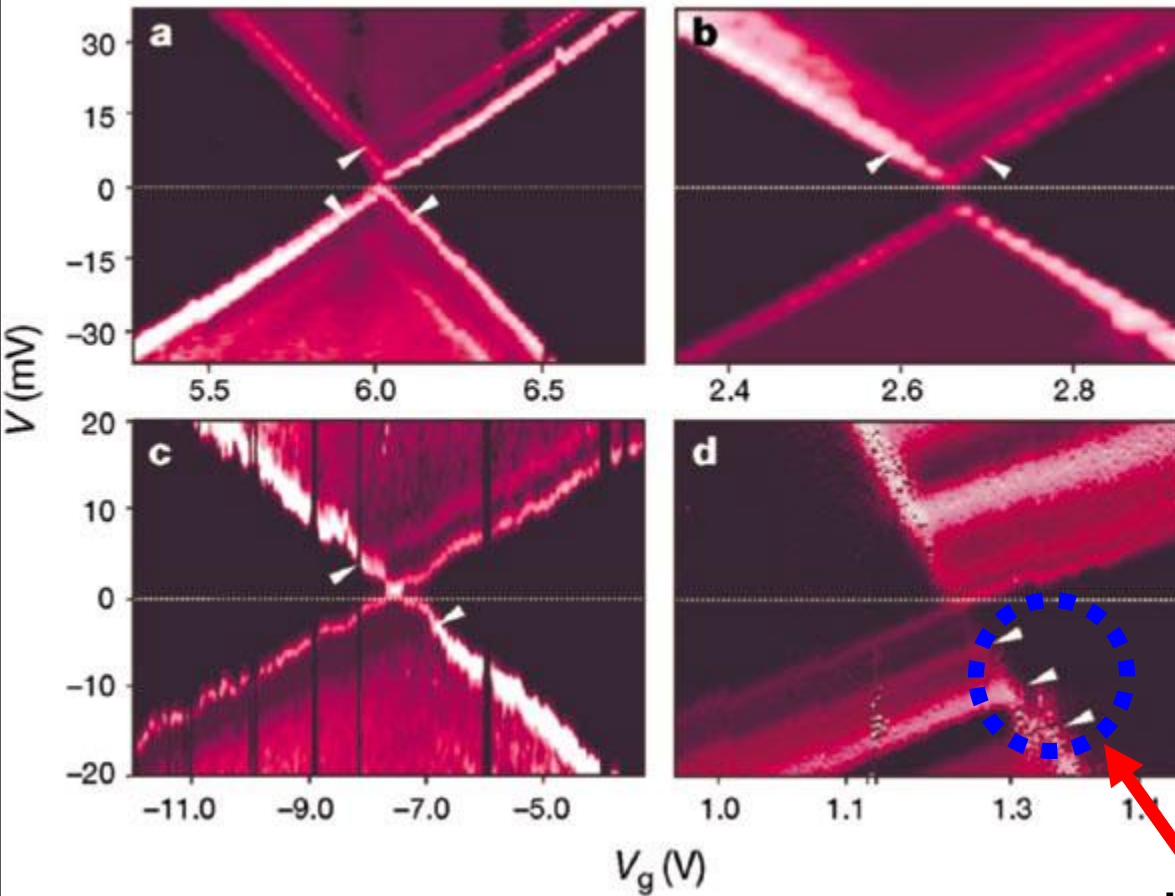


**Transmission coefficients
as functions of energy**

DFT + nonequilibrium Greens function

Magnetoresistance about 11%

Oscillator

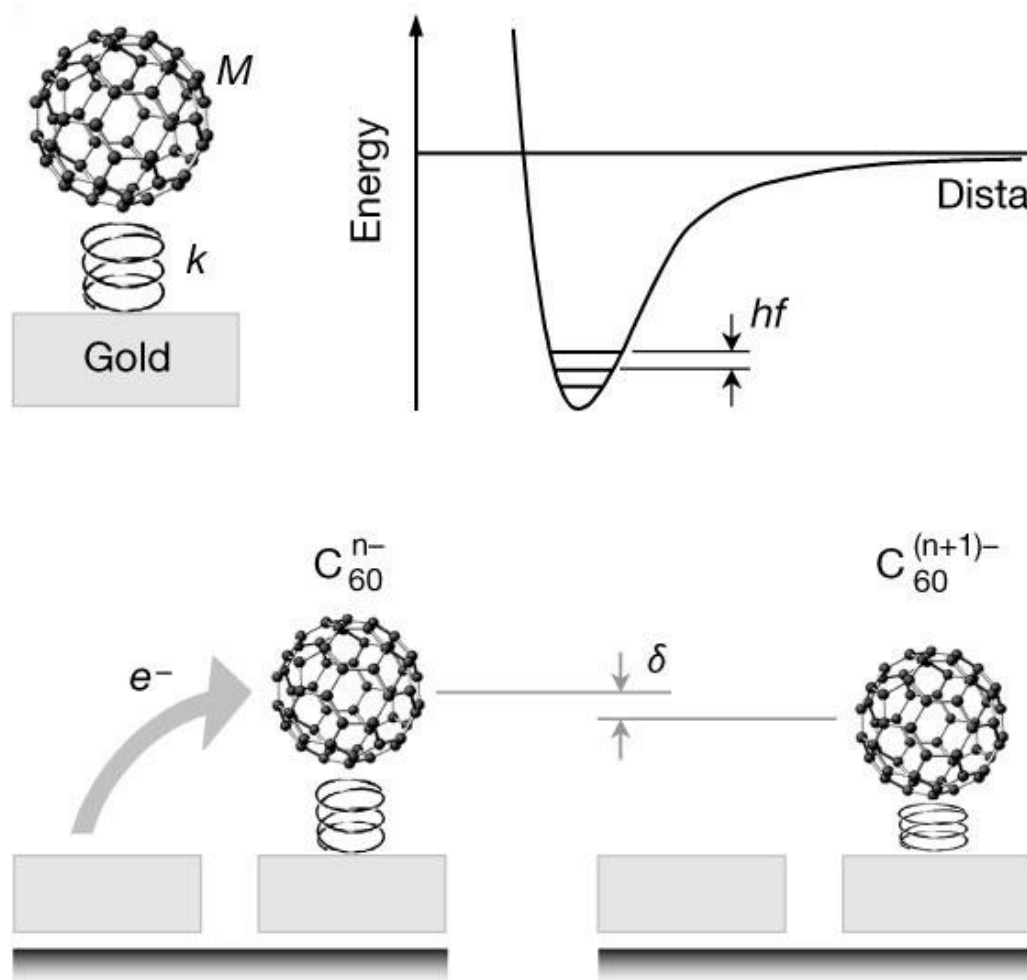


Au-C₆₀-Au system

Common feature
Quantized excitation with energy about 5meV

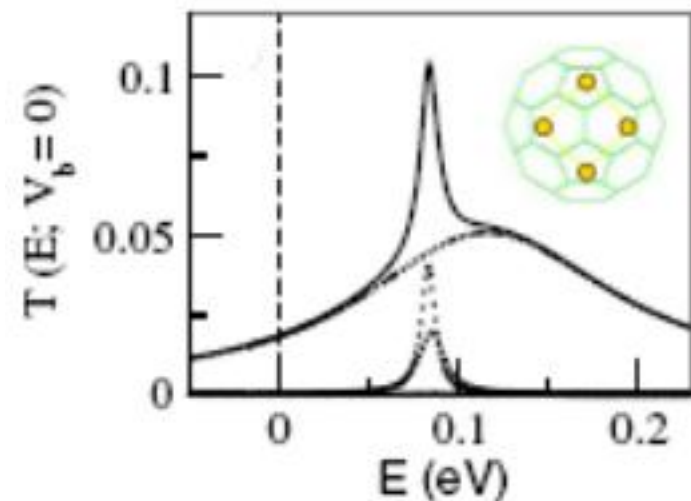
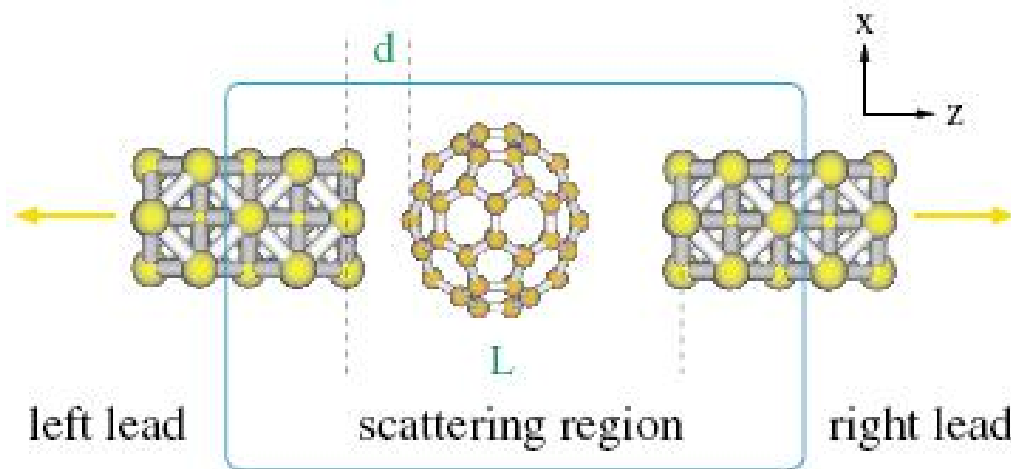
multiple excitation

Two-dimensional plots of dI/dV as a function of both V and V_g



- The excitation is interpreted as a centre-of-mass oscillation of C₆₀ within the confinement potential that binds it to the gold surface
- When an electron jumps on to C₆₀, the attractive interaction between the additional electron and its image charge on gold pulls the C₆₀ ion closer to the gold surface by the distance d . This electrostatic interaction results in the mechanical motion of C₆₀.

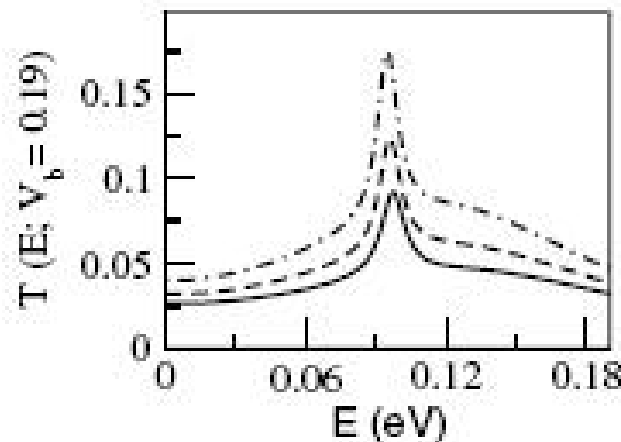
Diagram of the centre-of-mass oscillation of C₆₀



Schematic illustration of the molecular junction
Au-C60- Au system

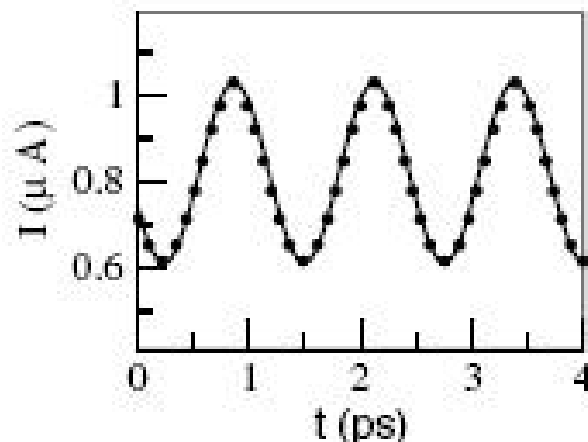
Transmission spectra

- Resonance inelastic conduction in molecular-scale electronics can be used to channel energy into a given mode of the molecular component to generate a desired motion.
- Dependence of the conductance properties on the molecular configuration leads to a time-modulated current whose temporal properties are subject to control.



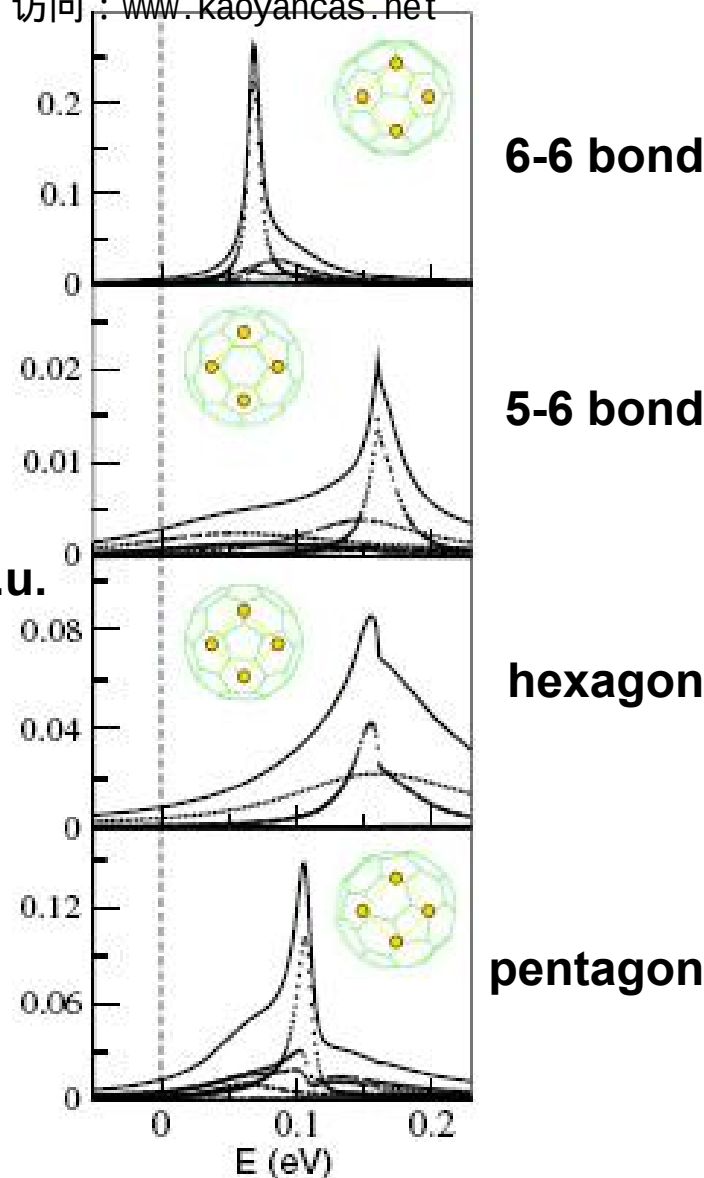
Transmission spectra for different C_{60} location:
 $d=5.05$ (solid), 5.13 (dashed) and 5.23 (dot-dash) a.u.

Location dependent



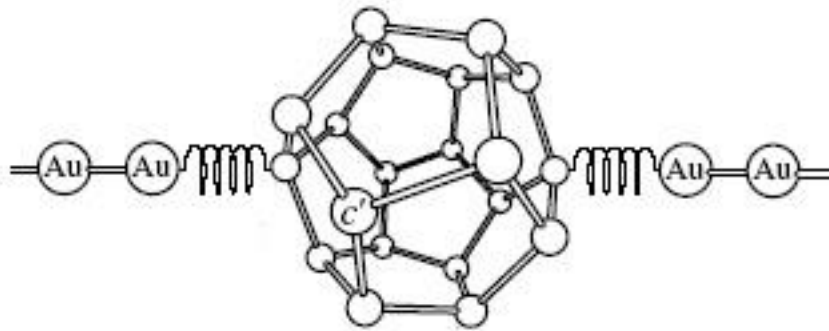
Spontaneously oscillating current vs time

A nanoscale generator of ac electromagnetic field
 (frequency 0.8 THz; ac/dc ratio 0.26)

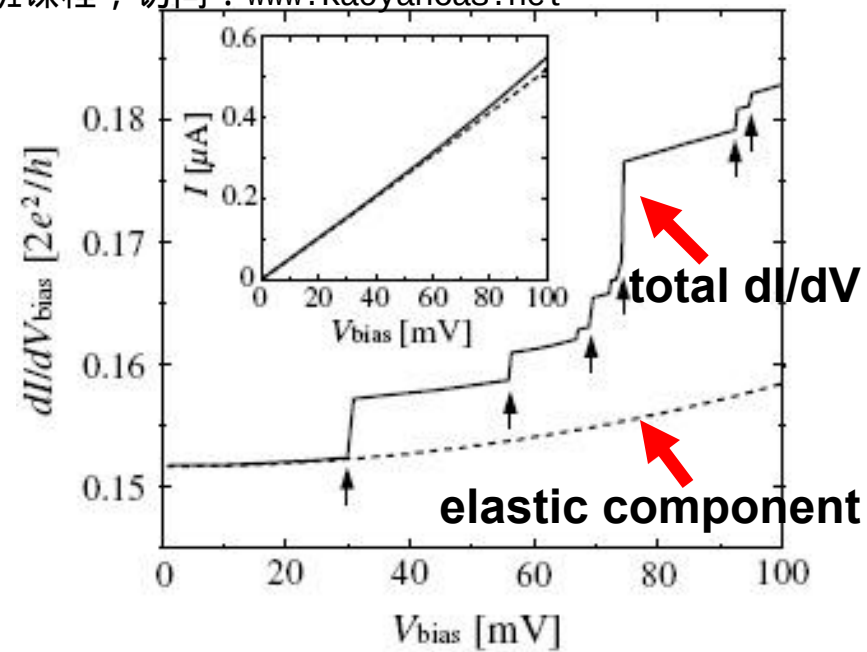


Transmission spectra for different C_{60} orientation

Orientation dependent

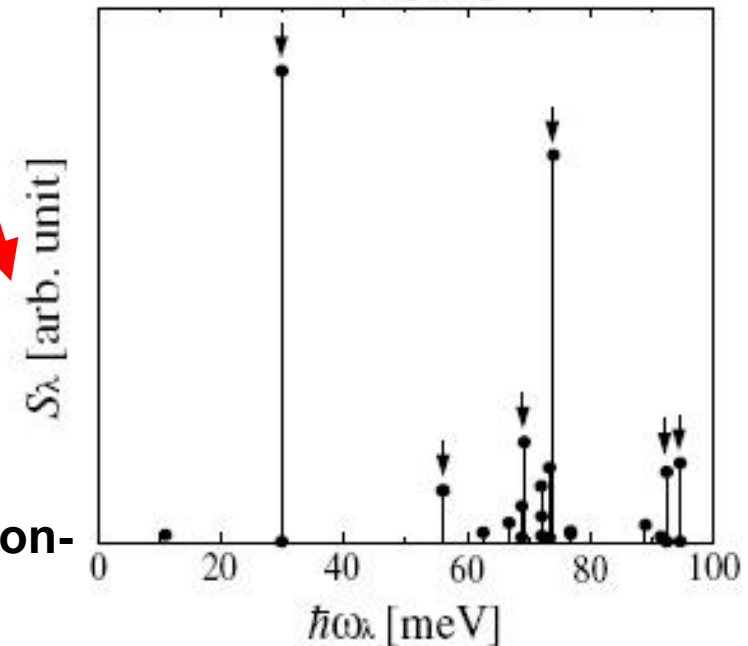


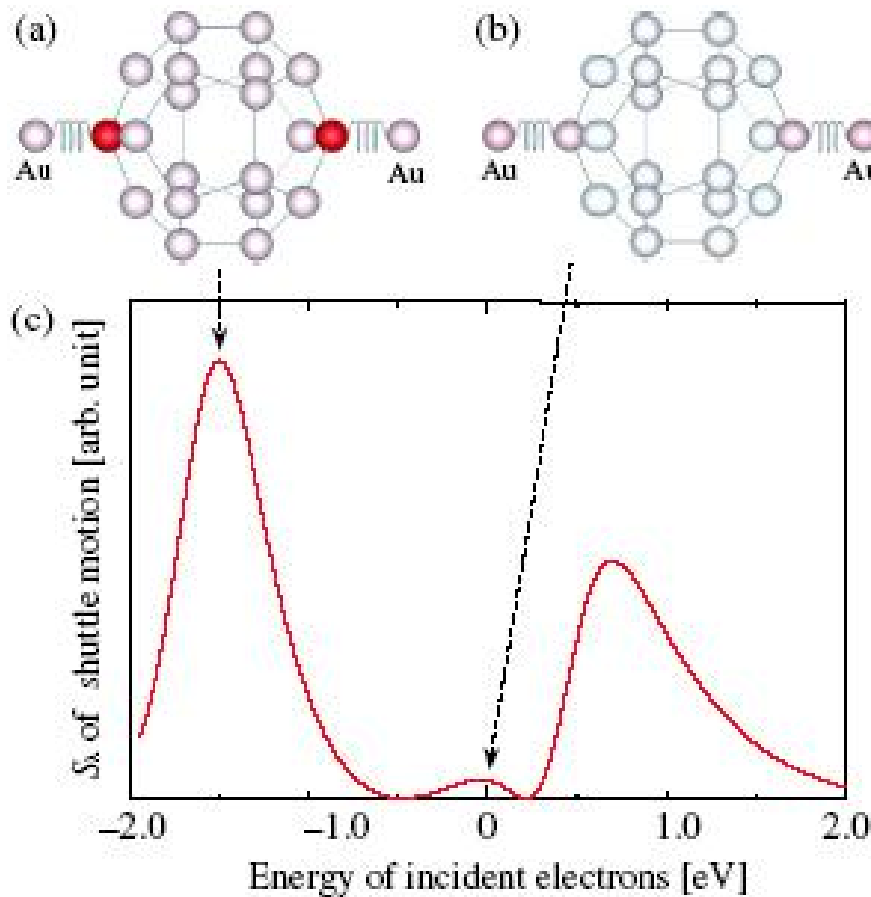
Schematic diagram of **Au- C₂₀- Au system**



Scattering intensity due to molecular vibrations

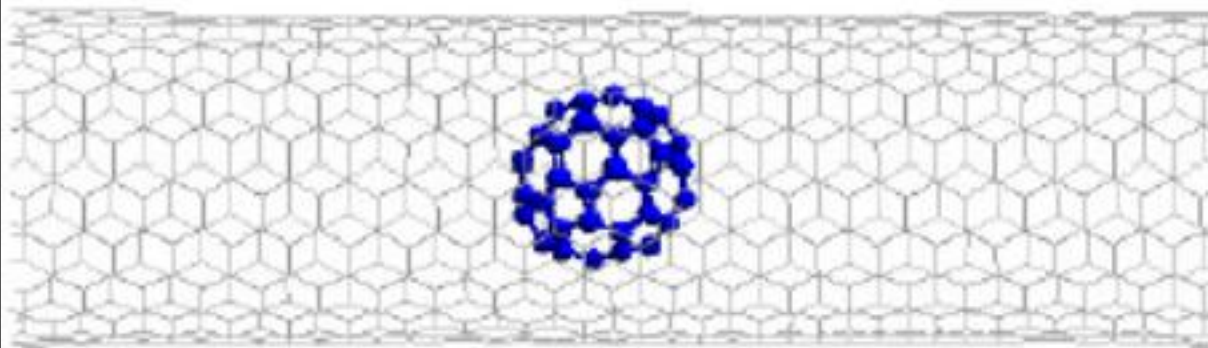
- Large discontinuous steps appear in the dI/dV curve when the applied bias voltage matches particular vibrational energies.
- The magnitude of the step varies with the vibrational mode and to depend on the local electronic states besides the strength of electron-vibration coupling.



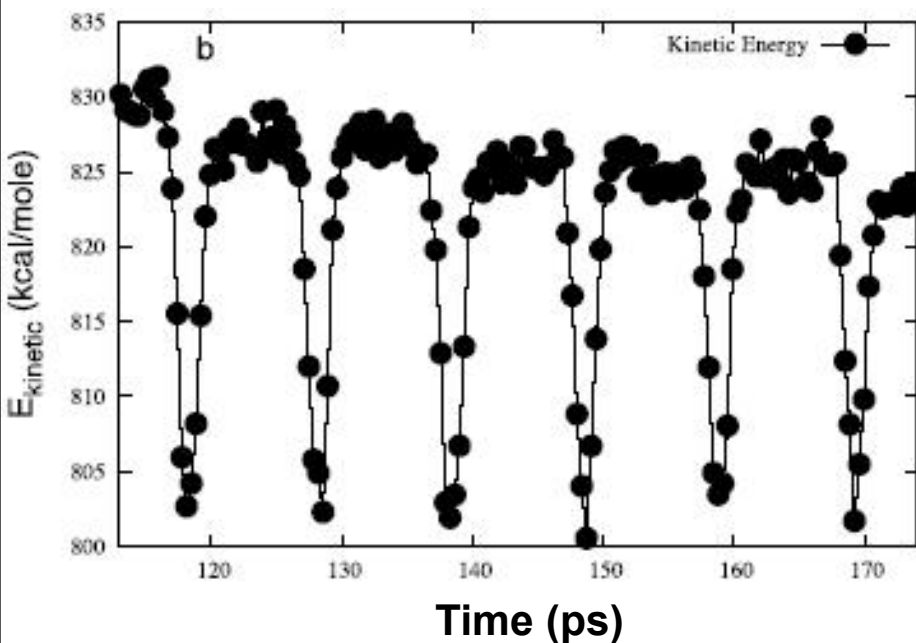


The electron density of Au-C₂₀-Au at (a) -1.5 eV and (b) 0 eV (the Fermi level), and (c) the scattering intensity for the shuttle motion of C₂₀. The electron density is indicated by the red shading on the atom spheres.

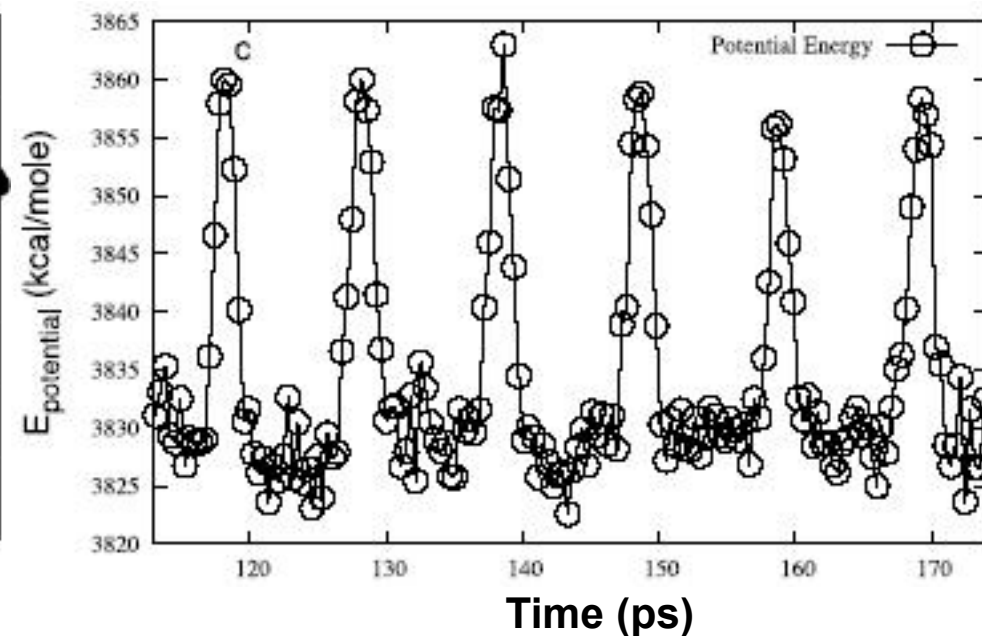
- The excitation rate is expected to increase significantly when the electronic state localized at C atoms adjacent to Au electrodes lie close to the Fermi level.
- Such a localized state lies 1.5 eV below the Fermi level ($E_F = 0$ eV), and the scattering intensity of the shuttle motion exhibits a maximum peak at -1.5 eV.
- The excitation rate can be enhanced by tuning the gate voltage to shift the localized state to the Fermi level.



Structure model of the novel oscillator. One C60 molecule is inside a (10, 10) SWNT of length 50.05 Angstroms



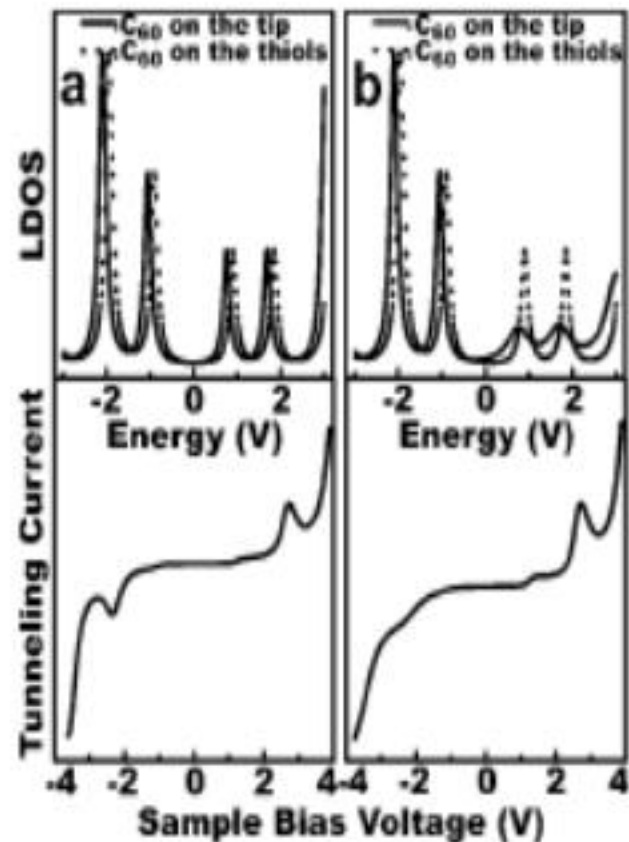
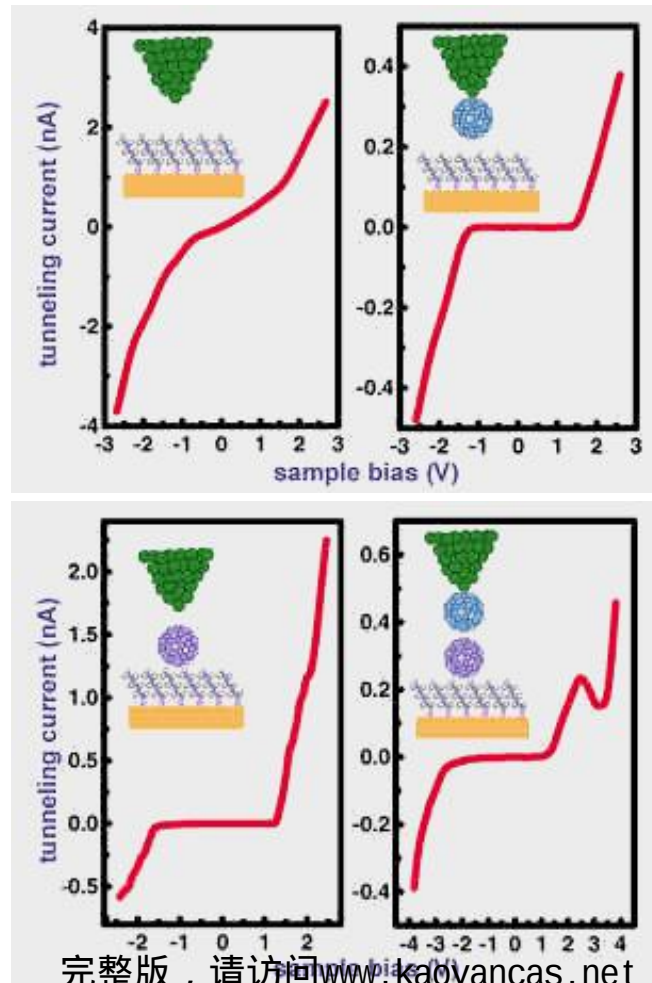
Evolution of buckyball kinetic energy between 120 and 170 ps



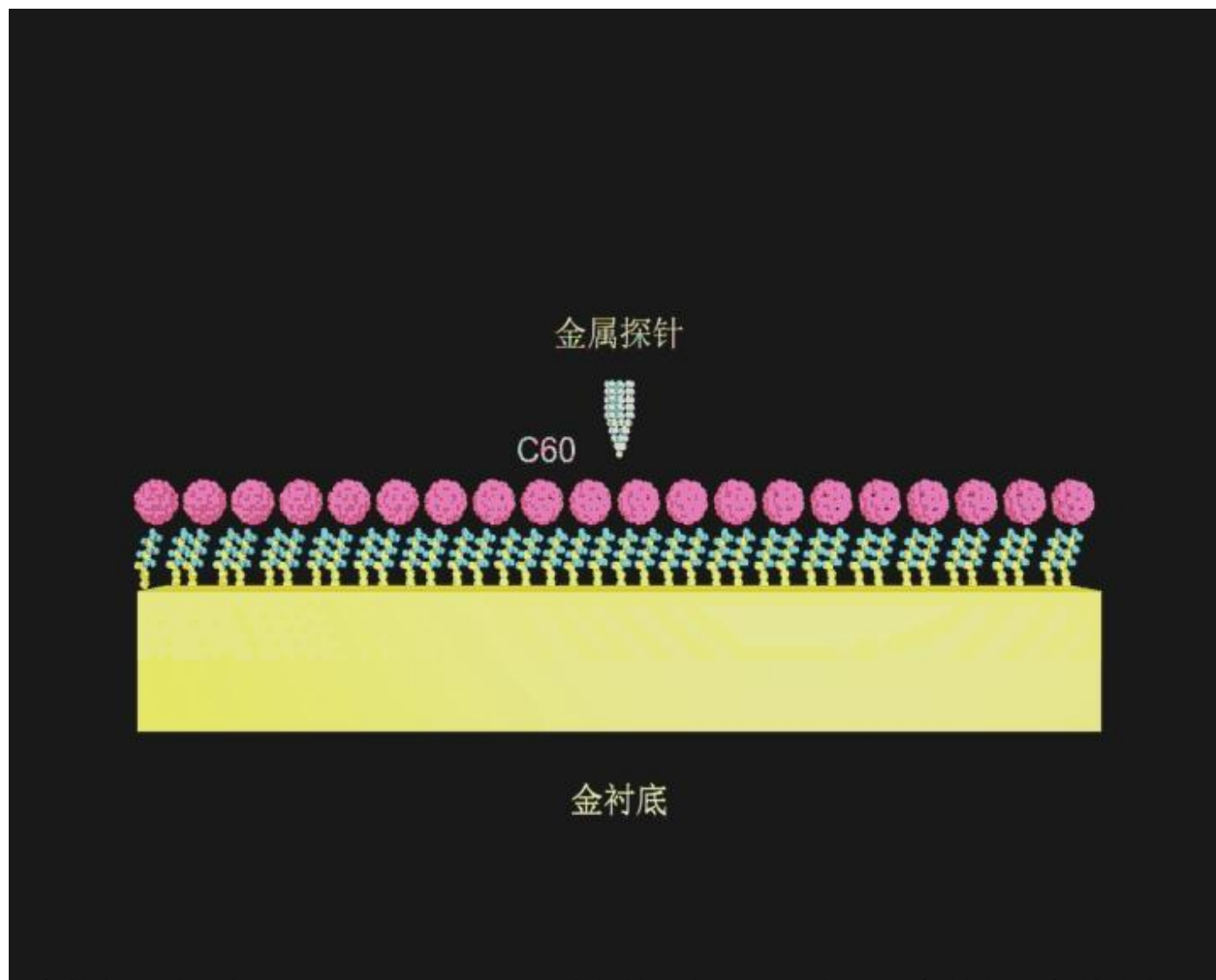
Evolution of potential energy of buckyball between 120 and 170 ps

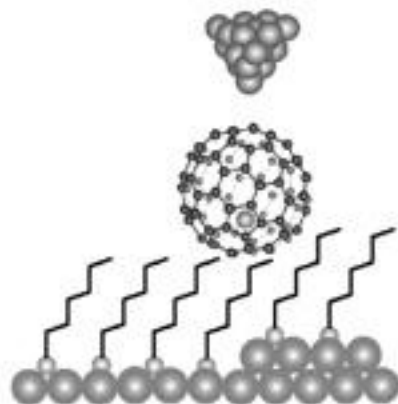
NDR

Negative differential-resistance device involving two C₆₀ molecules
C.G.Zeng *et al.*, Appl.Phys.Lett. 77,3595(2000)



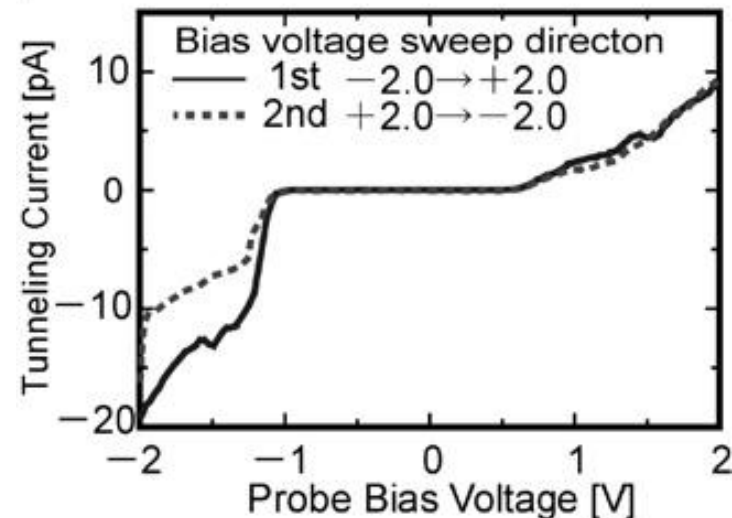
NDR molecular device involving two C_{60} molecules



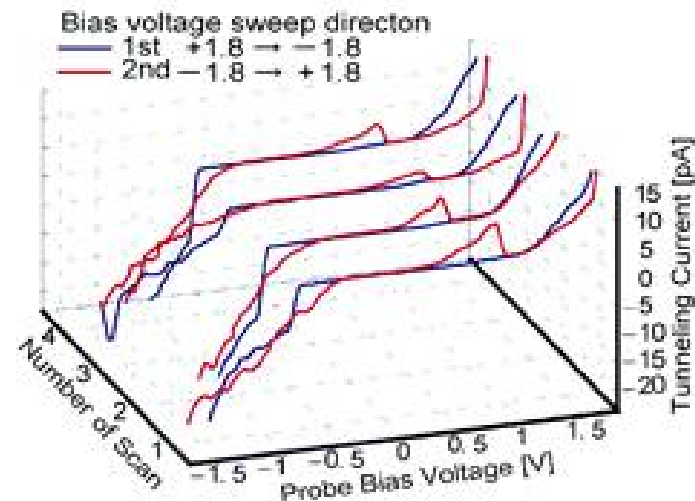


Tb@C₈₂ system

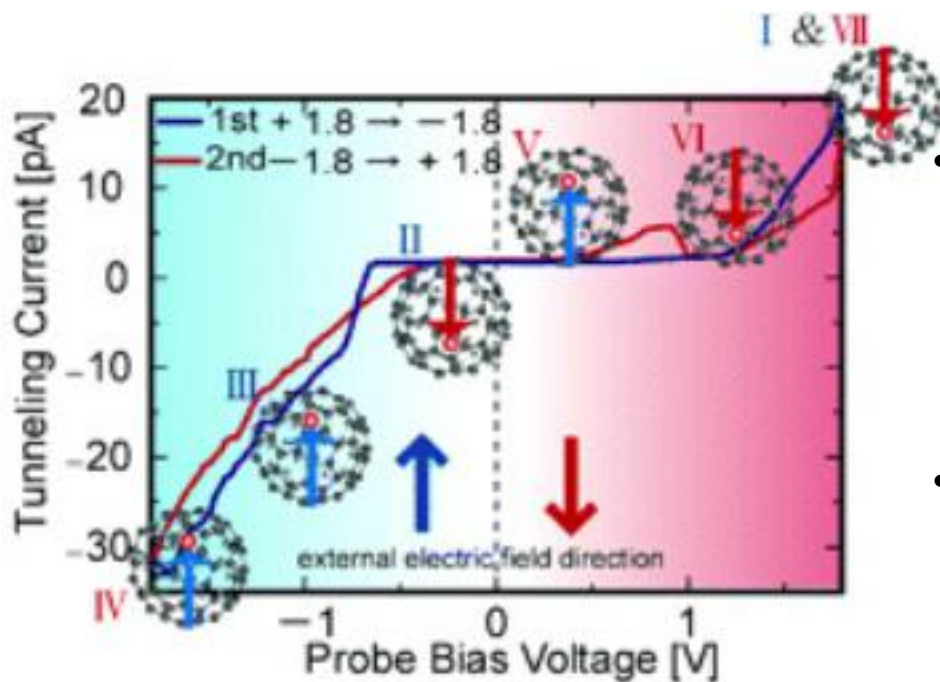
- The I-V curve shows no negative differential conductance (NDC) at T=65K
- NDC is observed in the I-V curve at T=13 K



I-V curve at T=68 K

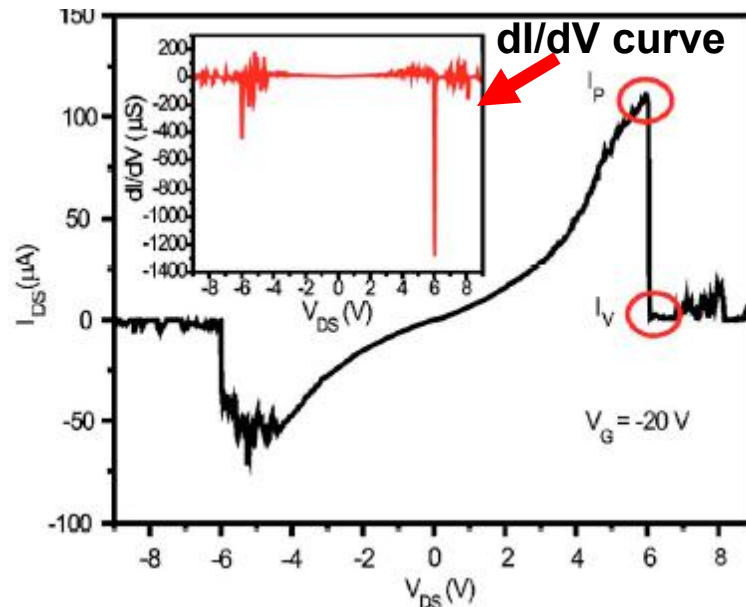


I-V curve at T=13 K



- NDC here is interpreted in terms of a switching of the Tb@C_{82} molecular orientation caused by the interaction between its electric dipole moment and an external electric field.
- At higher temperature, the electric dipole moment of the Tb@C_{82} molecule tend to be oriented at random by thermal energy, so no NDR appears.

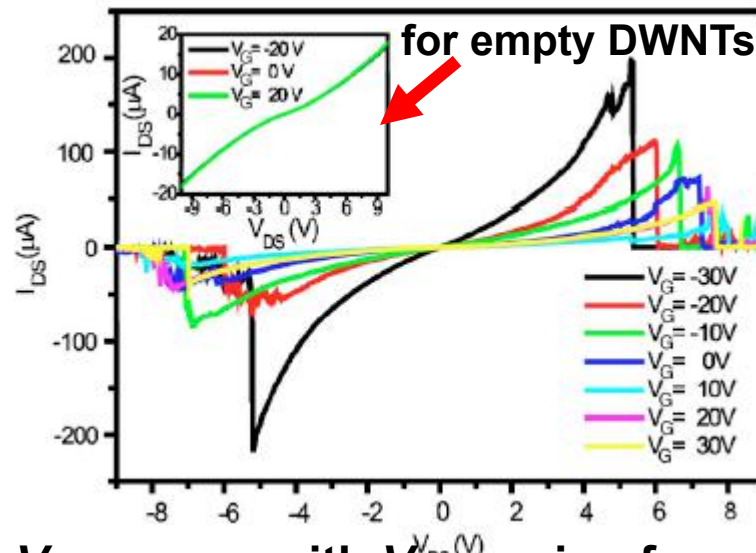
Candidate schematic image of single molecular orientation switching of Tb@C_{82}



C₆₀-filled DWNT

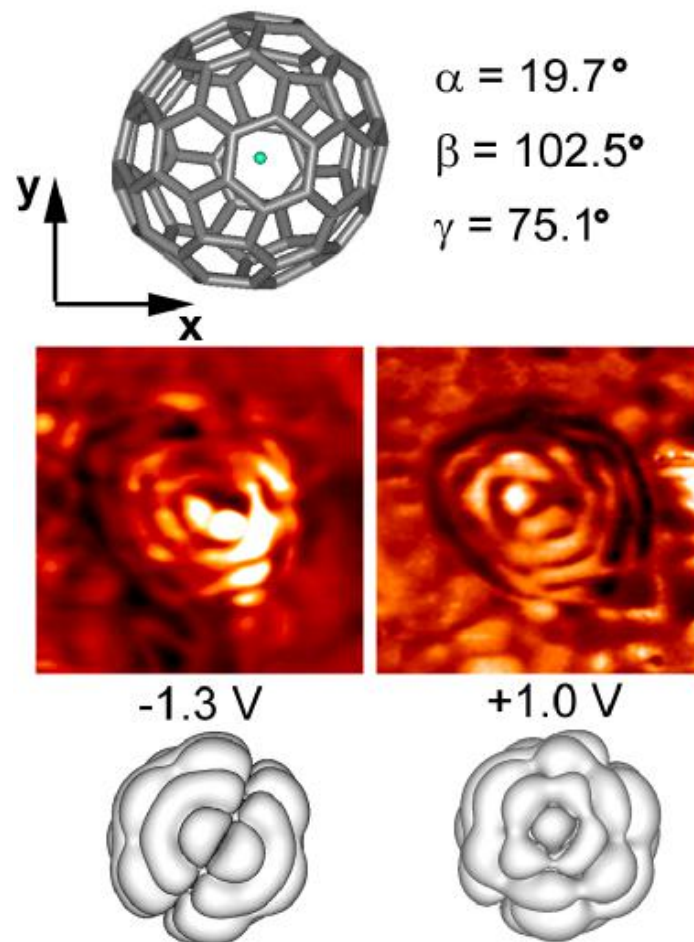
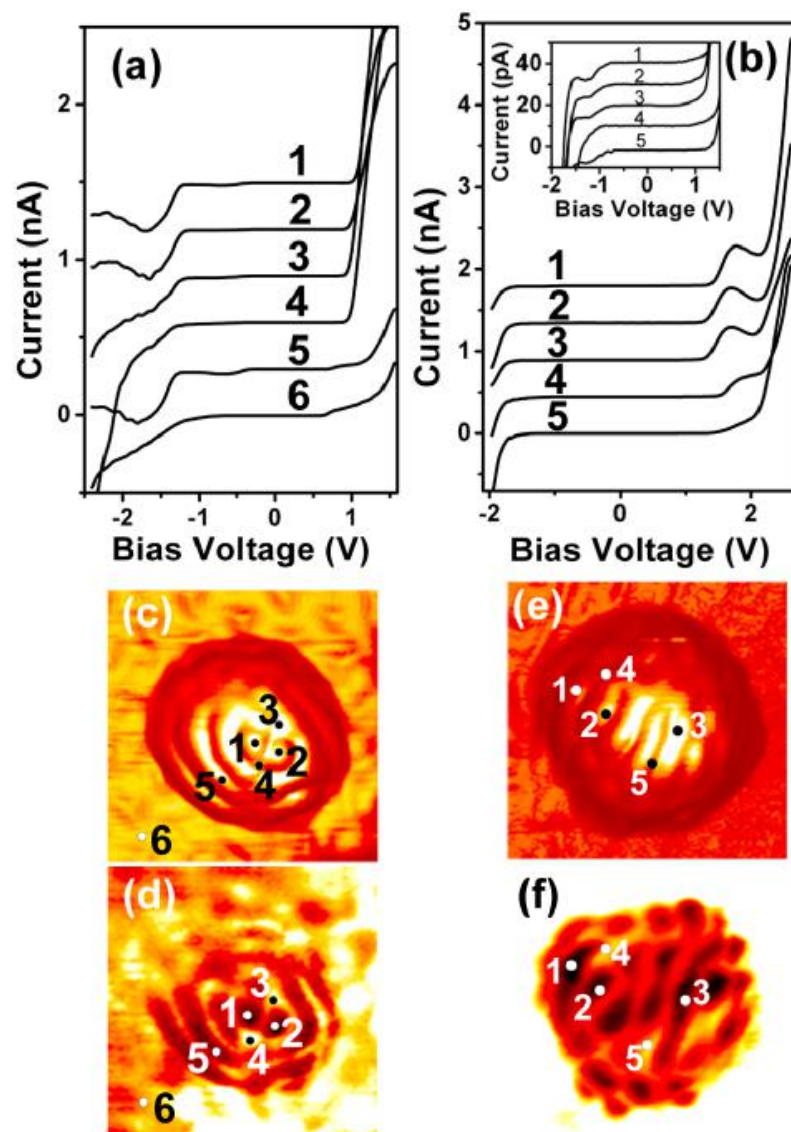
- peak-to-valley current ratio is about 1300
- Gate voltage dependence characteristics of I_{DS} - V_{DS} curves indicates that a threshold voltage V_{th} for the appearance of current peak is greatly affected by gate voltage.
- NDR characteristic is symmetrical

I_{DS} - V_{DS} curve $V_G = -20 V$ at RT

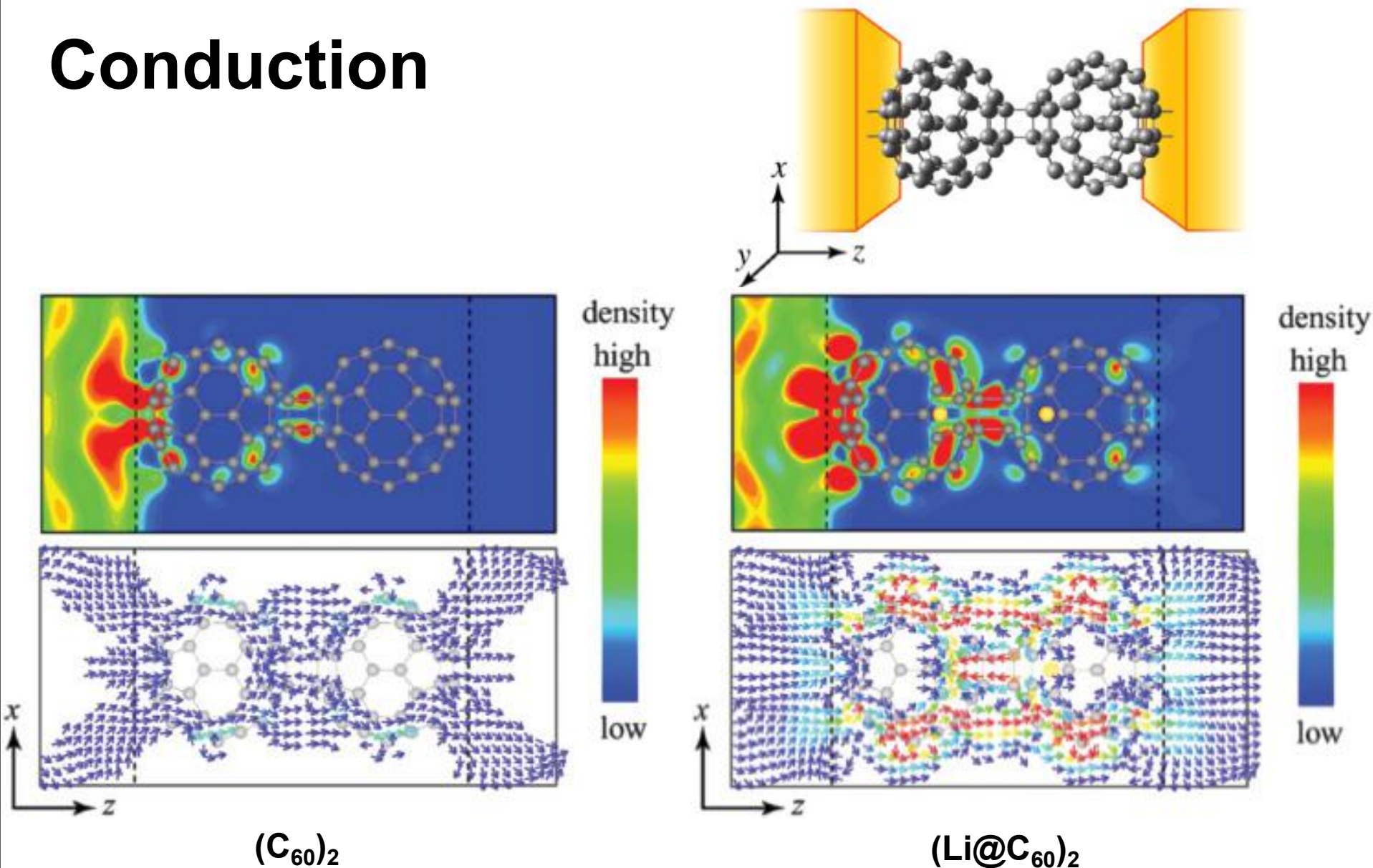


I_{DS} - V_{DS} curves with V_G ranging from -30 to 30 V

NDR effect in Dy@C82 molecules



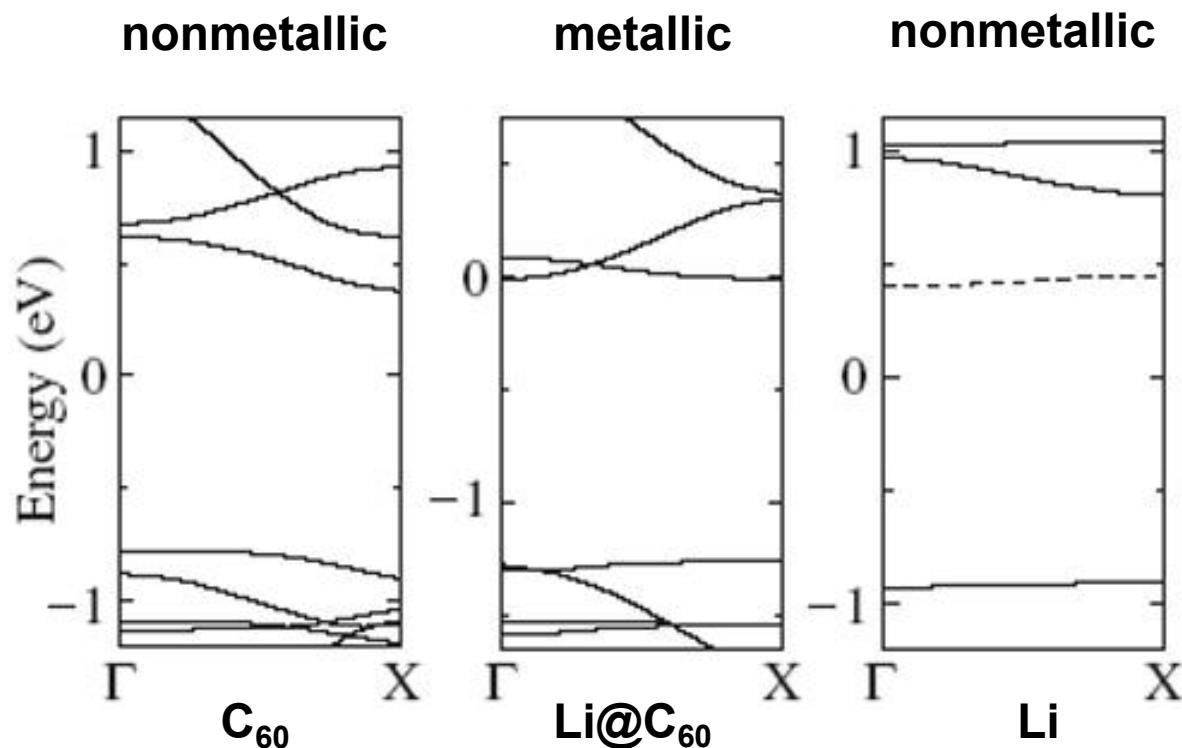
Conduction



Total charge density at Fermi level and total current distribution

完整版，请访问www.kaoyancas.net 科大科院考研网，专注于中科大、中科院考研

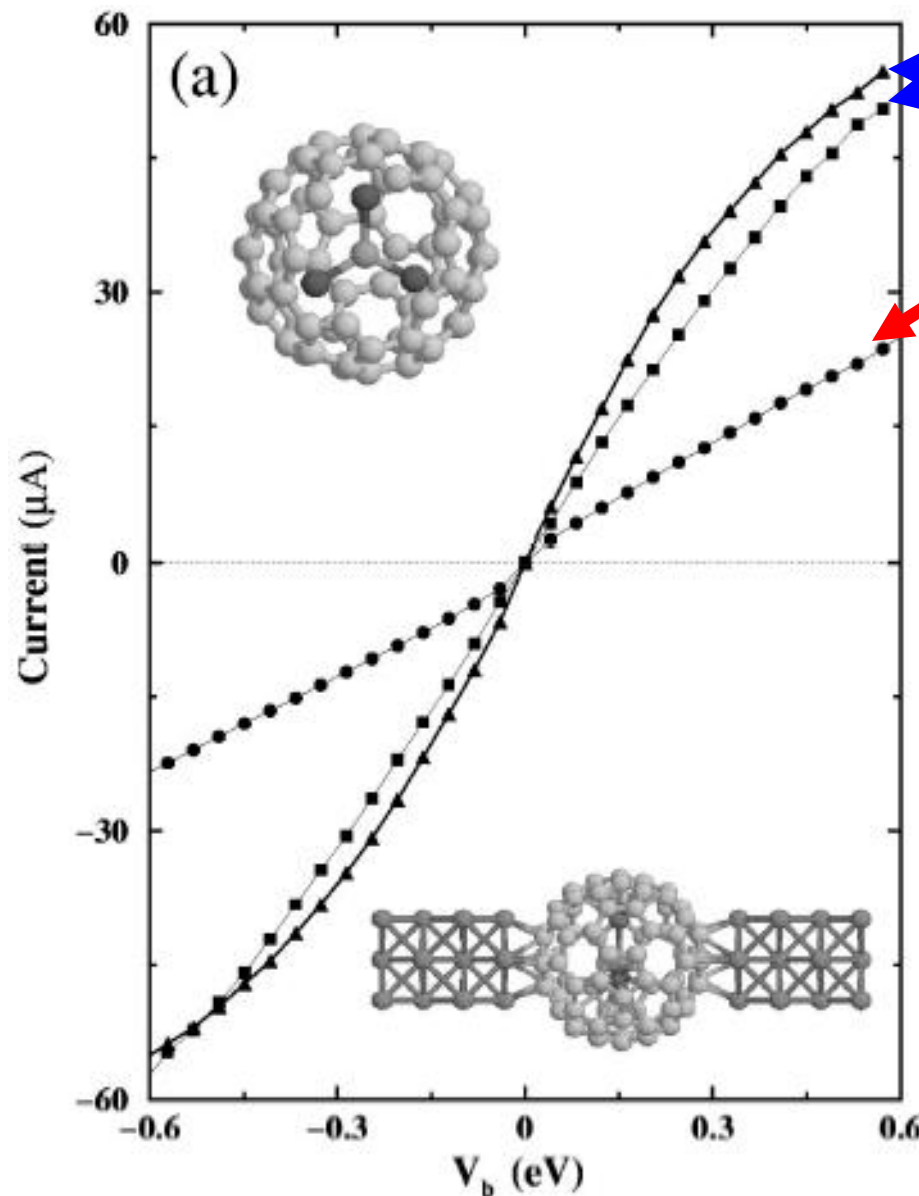
Tomoya Ono et al., PRL 98, 026804 (2007)



Energy band structures of chains with infinite length

As electrons are inserted into the fullerenes from inserting atoms, the unoccupied state around the junction is filled and the conductivity can be significantly improved.

	C_{60}	$(C_{60})_2$	$(Li@C_{60})_2$
$t_{u1,x}$	0.110	0.001	0.007
$t_{u1,y}$	0.133	0.012	0.020
$t_{u1,z}$	0.873	0.098	0.851



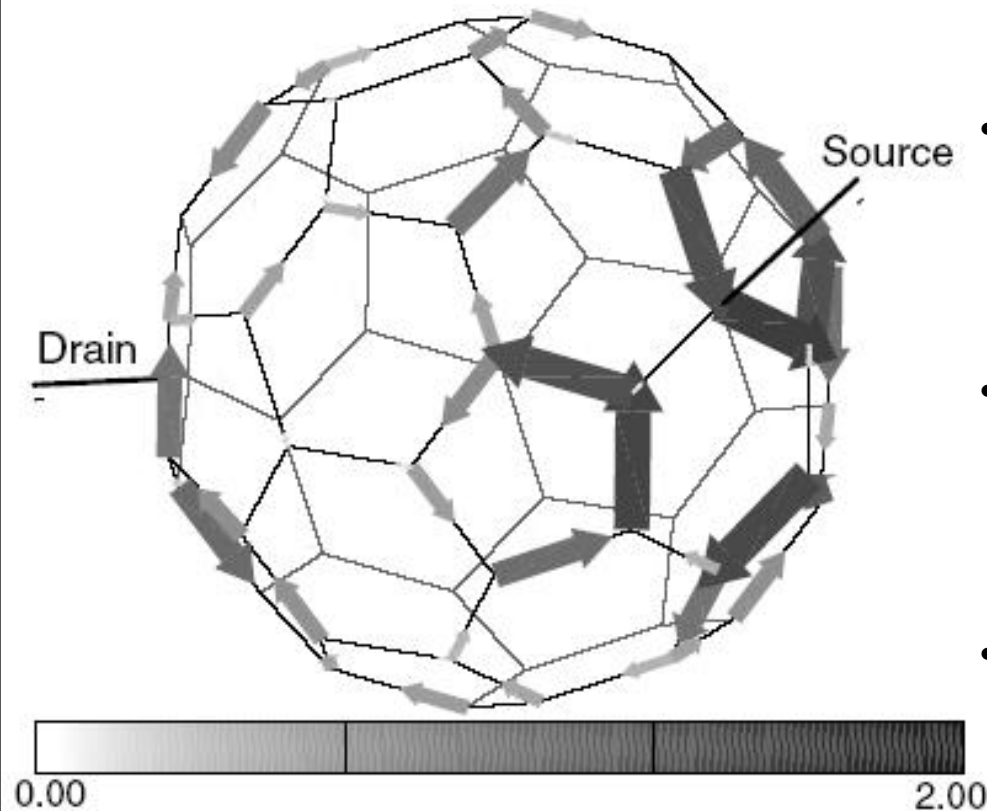
Al(100)-Sc₃N@C₈₀-Al(100)
device of two orientation

Al(100)-C₈₀-Al(100) system

NEGF-DFT method

- The current through the Sc₃N@C₈₀ device is double that through a bare C₈₀ device.
- The presence of the Sc₃N metal complex and its associated charge transfer to the C₈₀ cage aligns the level with the electrodes' Fermi level.

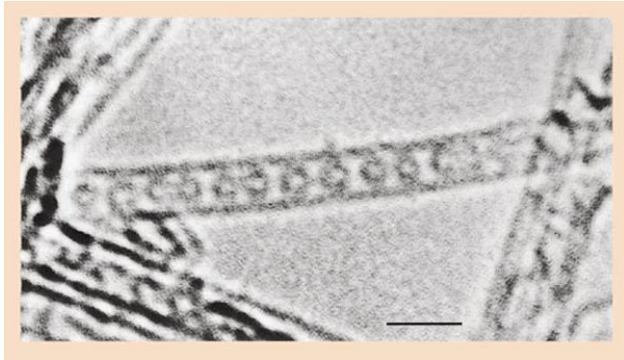
The I-V curves



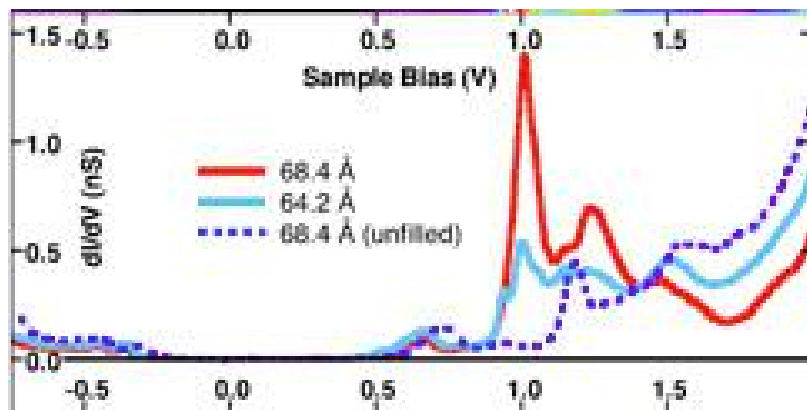
- The magnitude of the quantum loop current is much larger than that of the source-drain current I_{SD} .
- The direction of the magnetic moment associated with this loop current is reversed if the electron energy is swept across the resonant levels.
- Under certain conditions, the induced magnetic moment is restricted to a single particular plane regardless of the drain site for any fixed source position.
- These features could be applied, in principle, to **quantum mechanical devices** by using the quantum coupling to magnetic atoms.

Internal current distribution of the molecular bridge for the electron energy which is just below the LUMO of C_{60}

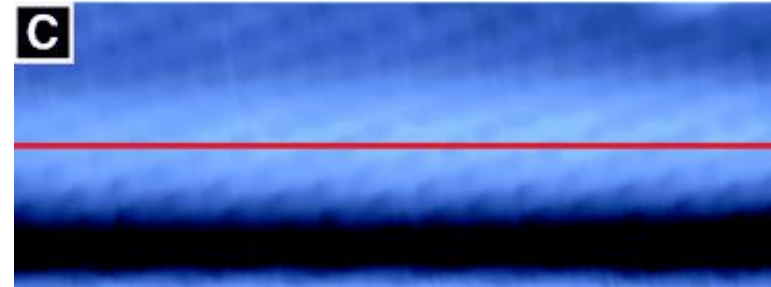
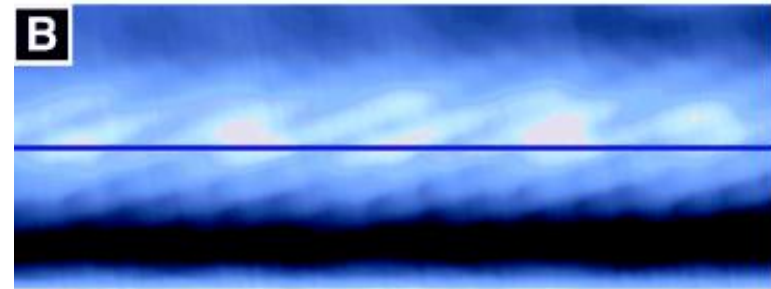
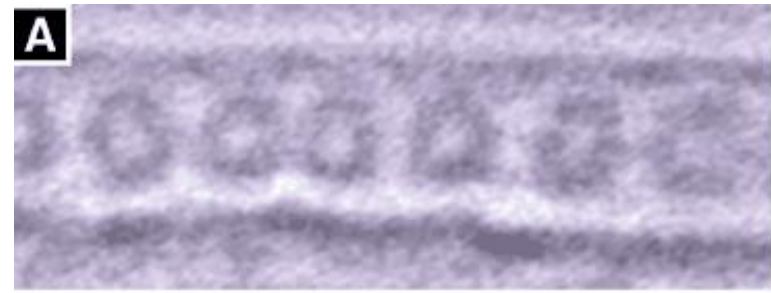
Peapod structure



HRTEM image of SWNT containing C_{60}
D. E. Luzzi *et al.*, Nature 396, 323 (1998)

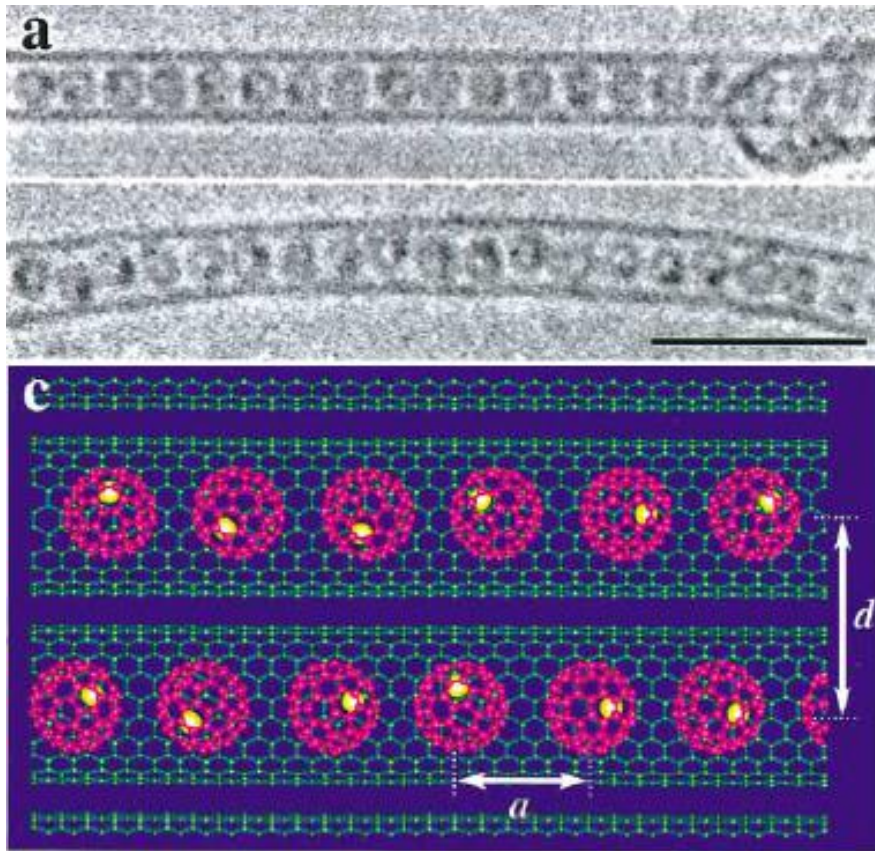


The dI/dV spectra (red and blue lines) at two locations. The dashed purple line is for spectra of SWNT without C_{60} .



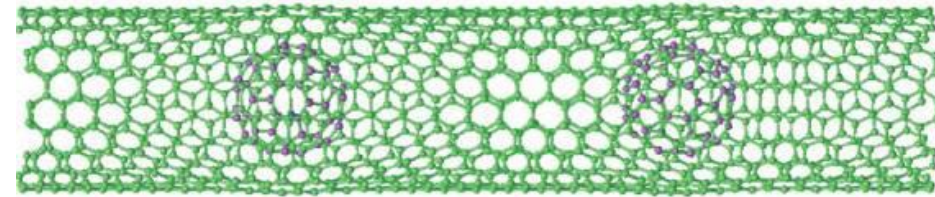
Structure and STM imaging of a peapod.
(b) +1.5V 700pA; (c) -1.5V 700pA

DOS are modified as C_{60} molecules are Encapsulated in SWNT at bias $> +1V$.

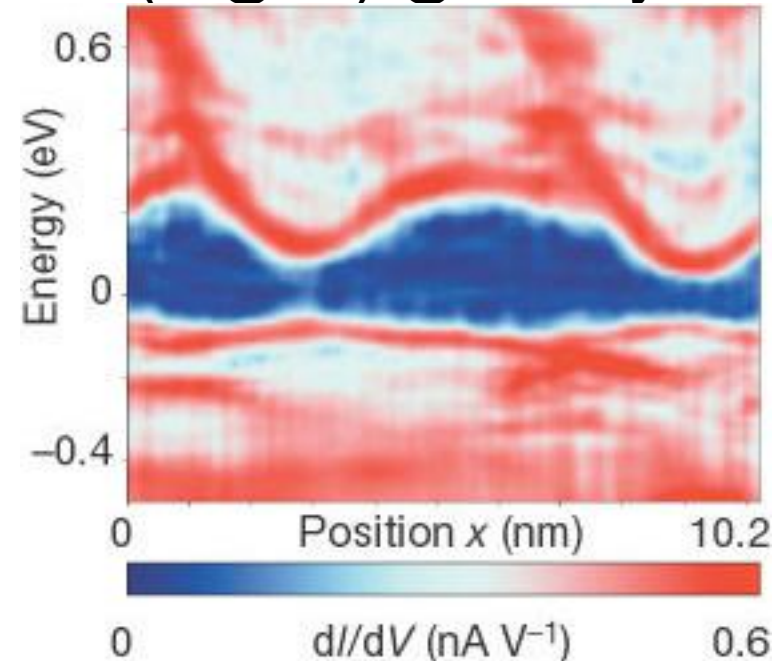


HRTEM images and schematic representation of $(\text{Gd}@C_{82})_n@SWNT$ s

The intermolecular distance between $\text{Gd}@C_{82}$ is extremely regular, regarding the chains of $\text{Gd}@C_{82}$ as novel **one-dimensional crystals**.



$(\text{Gd}@C_{82})_n@SWNT$ system

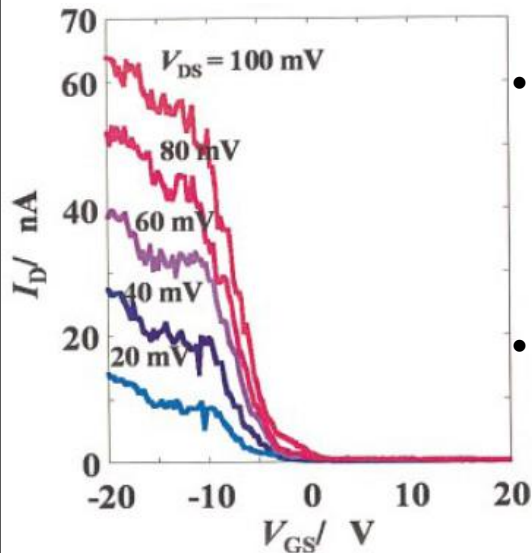
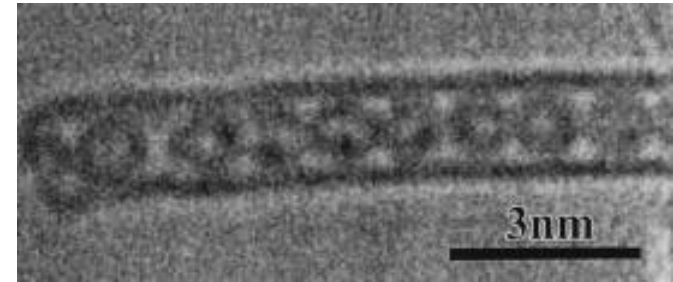


The dI/dV spectra taken along the 10.2-nm-long GdMF-SWNT

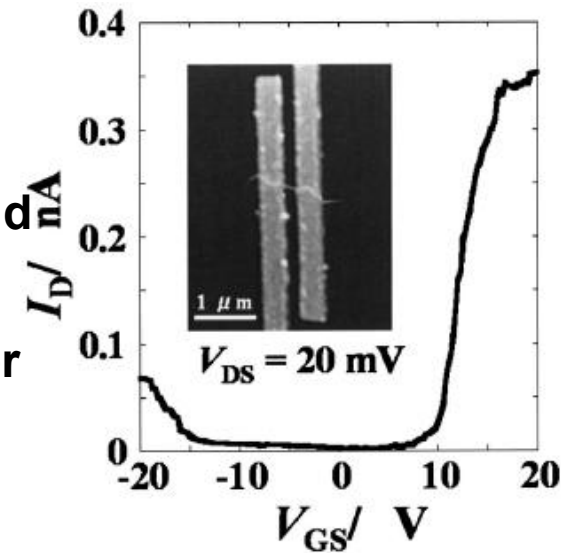
Band gap of 0.5 eV is **narrowed** down to 0.1 eV at sites where endohedral metallofullerenes are inserted

Field-effect transistor

HRTEM image of an end cap part of an individual $\text{Gd}@C_{82}$ metallofullerene peapod



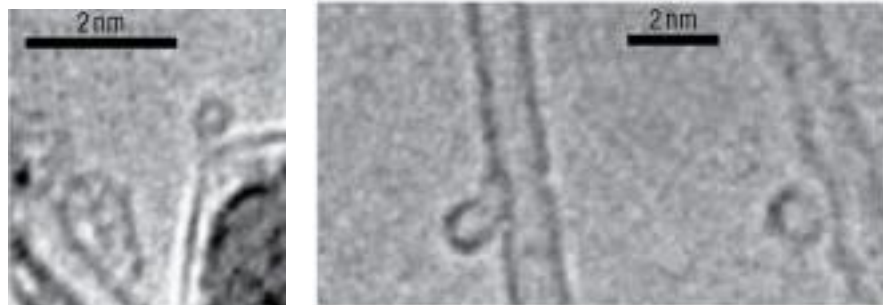
- C_{60} peapods exhibit unipolar *p*-type characteristics, whereas $\text{Gd}@C_{82}$ peapods show ambipolar both *p*- and *n*-type characteristics.
- This difference in transport behavior can be explained in terms of a band gap narrowing of the peapods.



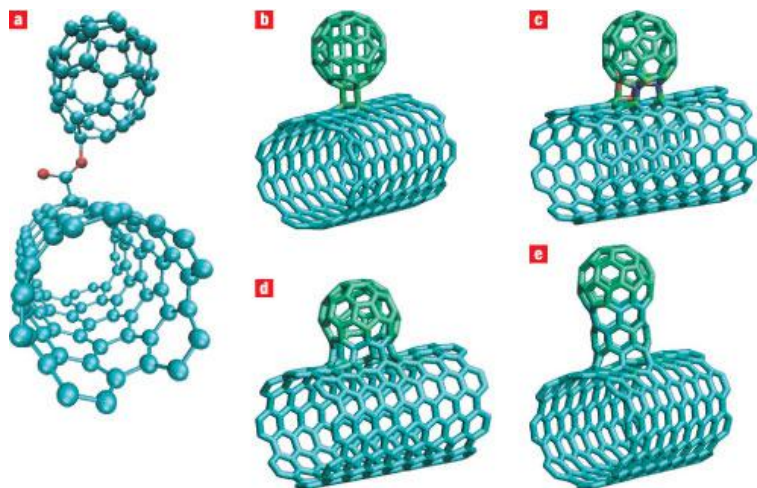
I_D - V_{GS} curves at different source-drain bias (V_{DS}) for C_{60} peapod

I_D - V_{GS} curves for $\text{Gd}@C_{82}$ metallofullerene peapod

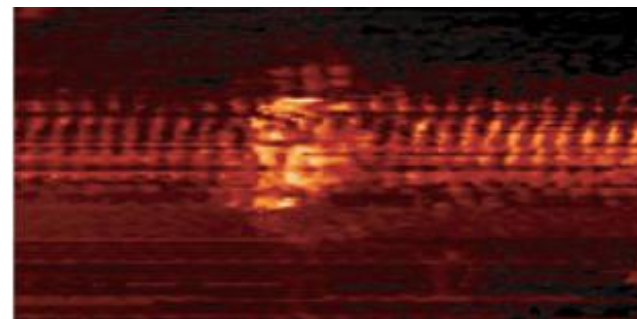
Field-emission characteristics of NanoBuds



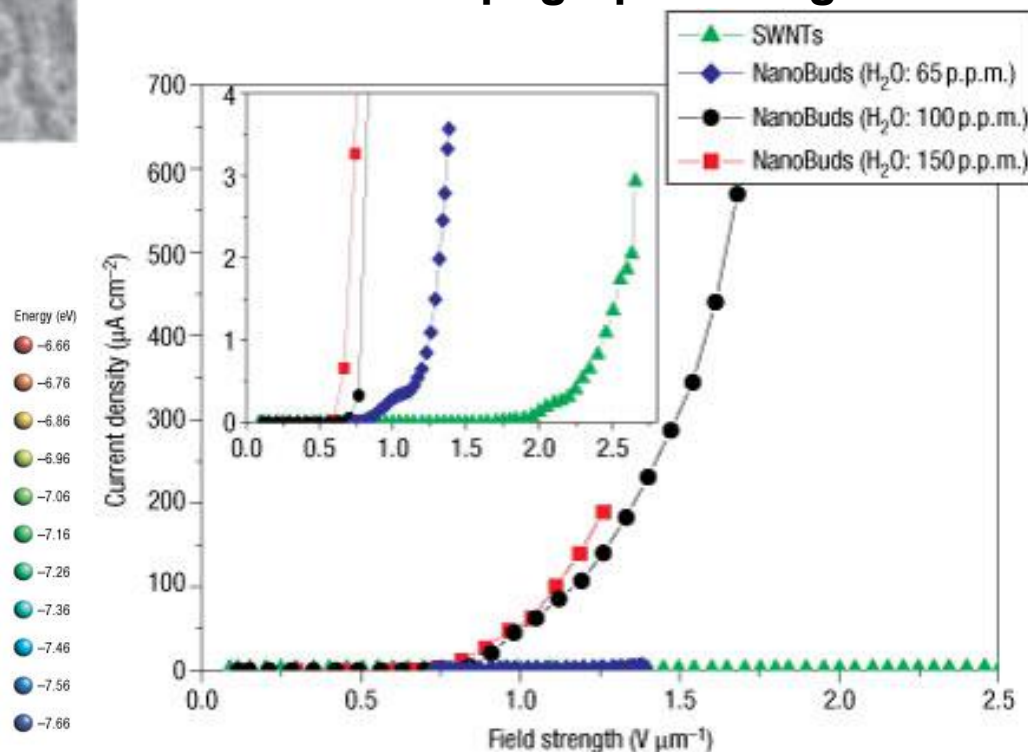
High-resolution TEM images



Bonding scenarios of fullerenes on SWNTs



STM topographic image



Comparison of current density against electric field strength of NanoBuds with SWNTs

(4). 金属团簇

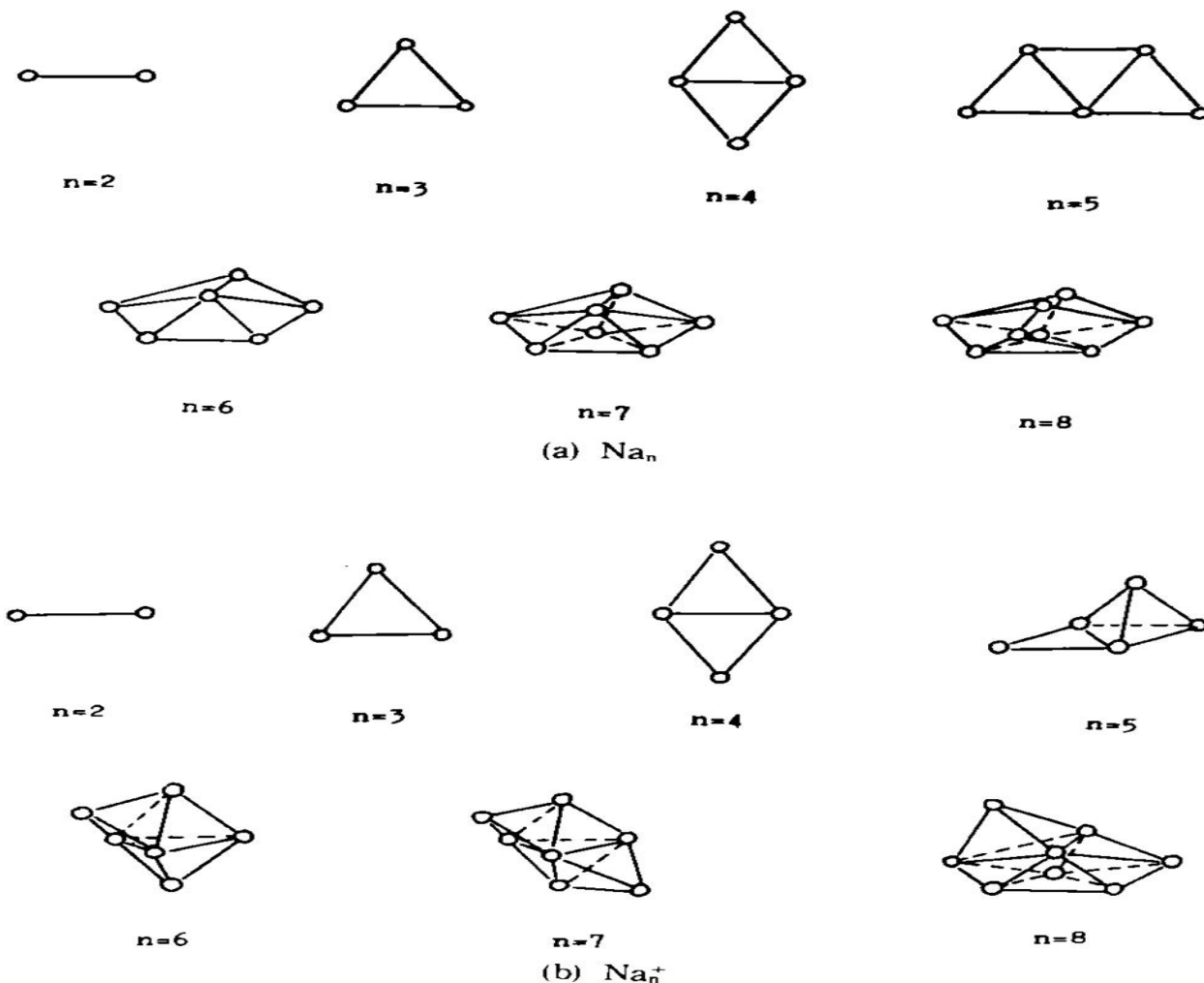


图 17 团簇 Na_n 和 Na_n^+ 的稳定结构

凝胶模型 动量序 起主导作用

正电荷密度均匀分布于 半径为 R 的球内：

$$n_+(r) = n_0 \theta(R - r) \quad n_0: \text{价电子密度}$$

利用电子密度参数 r_s ：

$$n_0 = \left(\frac{4\pi}{3} r_s^3\right)^{-1} \quad R = r_s N^{\frac{1}{3}}$$

Kohn - Sham 密度泛函方法：

$$n(r) = \sum_i |\psi_i(r)|^2$$

$$-\frac{1}{2} \nabla^2 \psi_i(r) + V_{\text{eff}}(r) \psi_i(r) = E_i \psi_i(r)$$

$$V_{\text{eff}}(r) = \varphi(r) + \mu_{xc}[n(r)]$$

$$\varphi(r) = -4\pi [n(r) - n_+(r)] / r$$

凝胶模型的结果对所有密度定性上是相同的。

在KS方程中，整个能量的主要贡献来自单电子本征值，其他部分的贡献与团簇结构分布无关。电子约束于球形凝胶区域导致壳层结构。

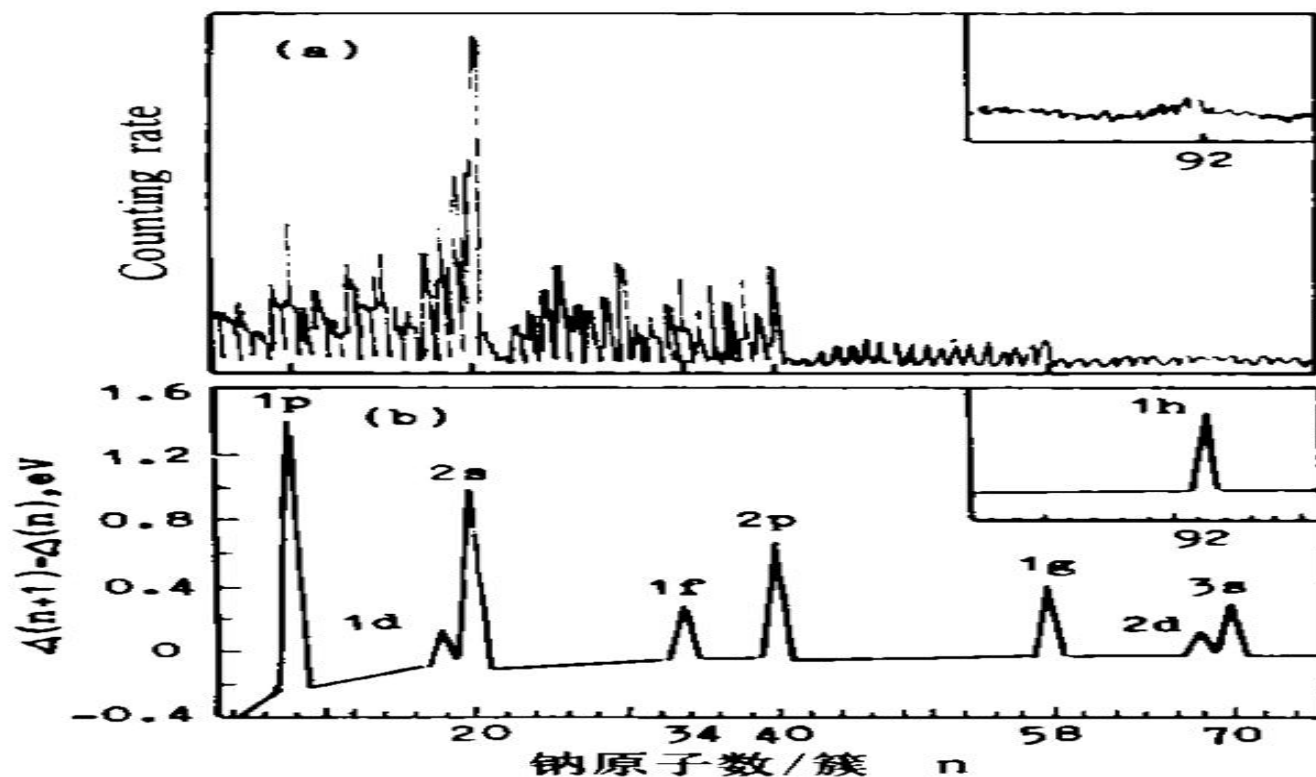


图 18 (a)超声喷注法产生钠团簇质谱^[28];
(b)相邻钠的团簇能量的二阶差分
 $\Delta_2(E)$ 随 n 的变化。

凝胶模型的能级 (n, l): $1s(2), 1p(6), 1d(10), 2s(2), 1f(14), 2p(6), 1g(18), 2d(10) \dots$

幻数: $2, 8, 18, 20, 34, 40, 56, 68, 70, 92, 106 \dots$

4. 团簇的自发破碎和库仑爆炸

当两个以上的电子从团簇上剥离后，团簇形成带多电荷离子簇。当团簇里的正电荷分布的库仑排斥超过团簇的束缚能，团簇会发生自发破碎，称为库仑爆炸→一种复杂的动力学过程。

多电荷离子团簇稳定性：存在一个临界原子数 N_c ，大于 N_c 才能稳定存在。

对Pb团簇： $Z=3$ ， $N_c=45$ ； $Z=4$ ， $N_c=72$

带负电荷的离子团簇也有库仑爆炸现象

5. 团簇的熔化与凝固、相变

有限体系，原子数目与热力学极限相距甚远。

如何定义？

熔点和凝固点不同 负比热

6. 团簇的磁学性质

磁性：

多数原子
有限分子

团簇

少量固体 (Fe, Co, Ni)

4d: 体材无磁性，部分团簇有磁性(Rh_N)

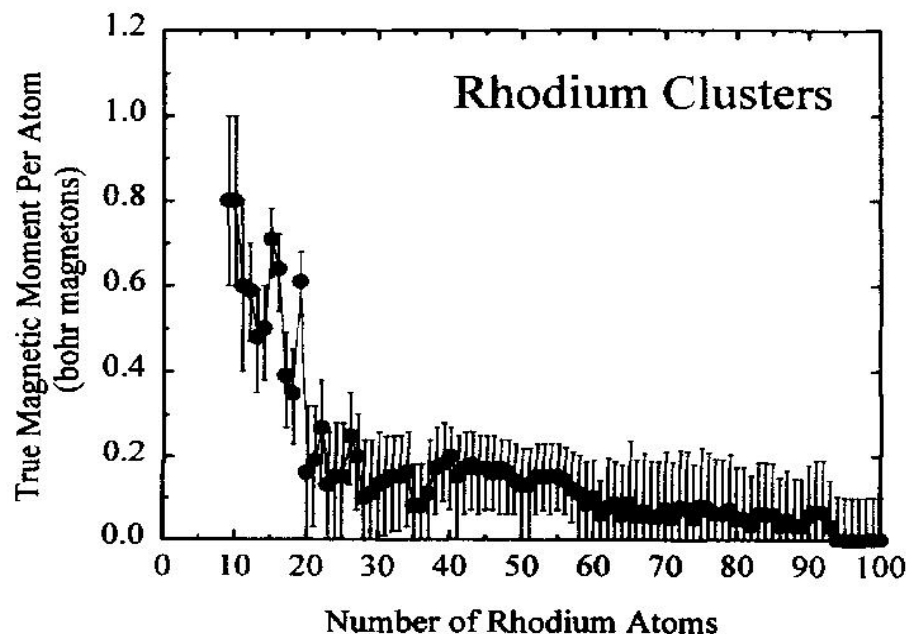


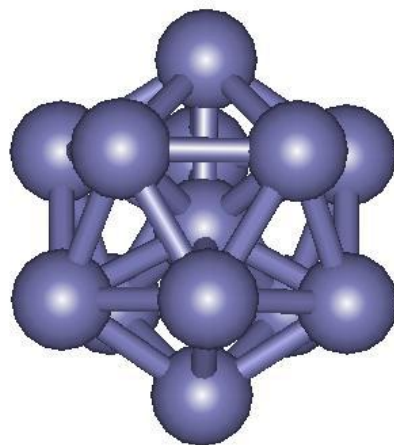
FIG. 1. Rhodium cluster magnetic moments per atom decrease with cluster size and are approximately zero, the bulk value for $n \geq 60$.

团簇的对称性愈高，其磁性就愈强？

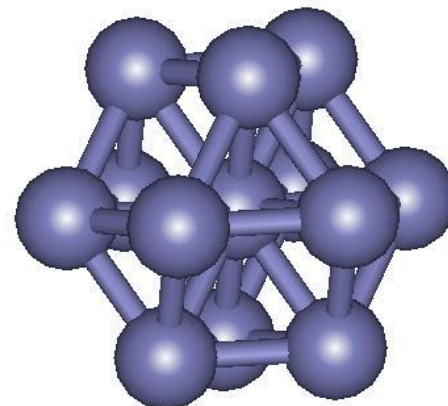
1994年前 Yes

1994年后 No

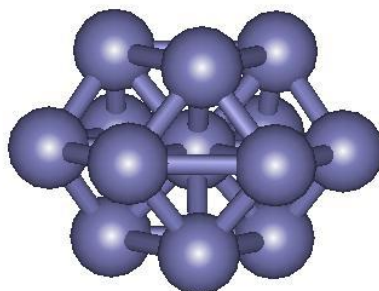
I_h



O_h



D_{3h}



Rh_{13}

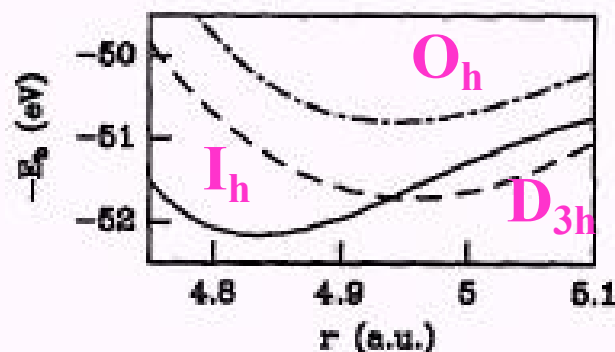


FIG. 1. Binding energies of the I_h (solid line), O_h (dot-dashed line), and D_{3h} (dashed line) Rh_{13} clusters vs the distance r between the central and surface atoms.

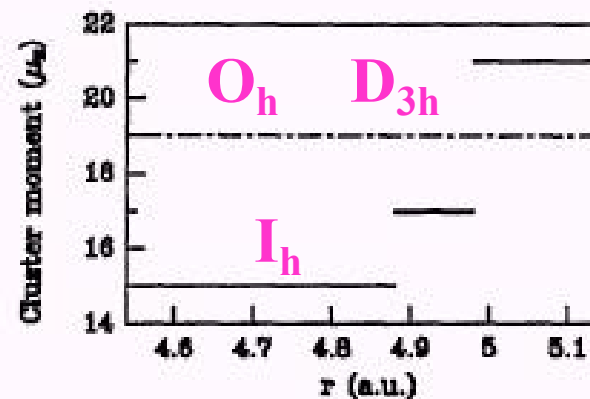


FIG. 2. The cluster moment as a function of r for the I_h Rh_{13} cluster (solid line), and for the O_h and D_{3h} Rh_{13} clusters (dot-dashed line).

$$\mu(I_h) < \mu(O_h) = \mu(D_{3h})$$

原因：多重磁性解

新观点：低对称性过渡金属团簇也可以具有比
高对称性团簇强得多的磁性。

7. 团簇的光学性质

三方面贡献：(1)孤立的原子性质；(2)原子与载体的界面；
(3)整个团簇的集体性质。

8. 金属团簇催化活性

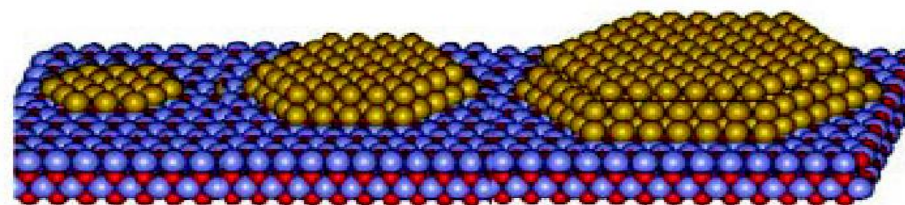
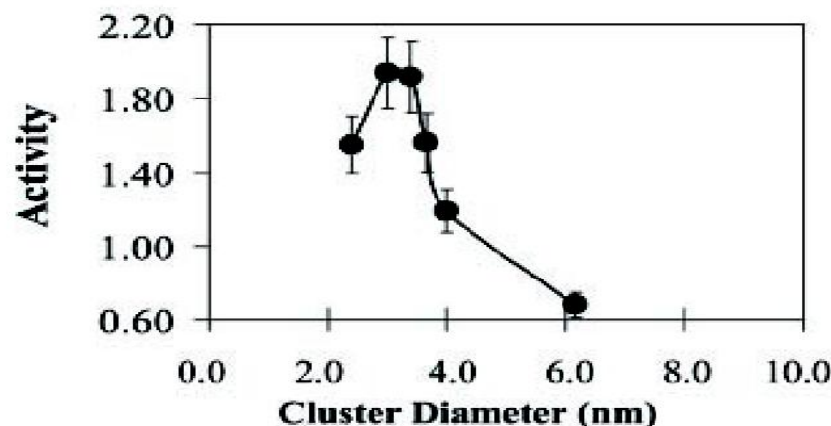
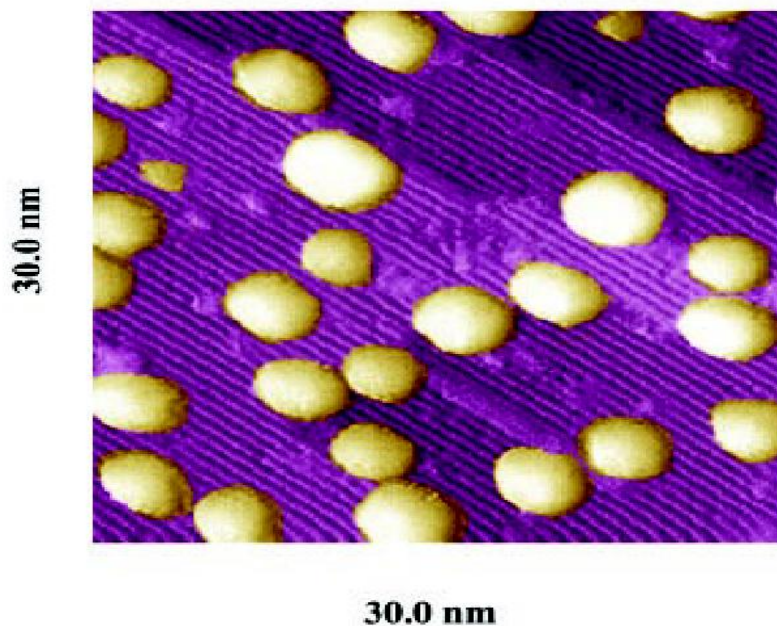


Fig. 2. Effects of particle size on the activity of titania-supported Au for the oxidation of CO (5).
完整版，请访问www.kaoyancas.net 科大科院考研网，专注于中科大、中科院考研

9. 团簇研究的前沿问题

(1) 澄清团簇的结构和力学、光学、电学、磁学等性质随所含原子数的变化规律。

(2) 研究团簇成核和形成过程及其规律，探索新的制备方法，以获得足够产额、尺寸均一和元素确定的团簇束流。

(3) 探索用尺寸和性质确定（若结构也能确定）的团簇，作为单元，在基体上组成团簇点阵的新型一维、二维和三维结构，研究束缚这些结构单元的量子特性及其在光电子学中的应用。

(4) 配位包裹团簇的价键结构和方式如何影响材料的性质？尺寸相当的团簇能否像蛋白质和病毒那样具有自组织性？

(5) C_{60} 及其衍生物的新组构，布基球-布基管-布基洋葱的电子属性和应用前景。 N_{20} ， P_{20} ， B_{32} 和金属碳球的稳定结构和性质。

(6) 在理论研究方面，要找寻新的理论方法或改造现有理论，使之不仅可预知团簇结构，模拟团簇动力学性质，而且能在实验中观察到，指导实验，研制新材料。

(7) 在实验技术上，不仅要发展有效的鉴定方法，直接确定小团簇 ($n < 100$) 中的原子位置，而且能对团簇表面进行控制、修饰、装配和裁剪。