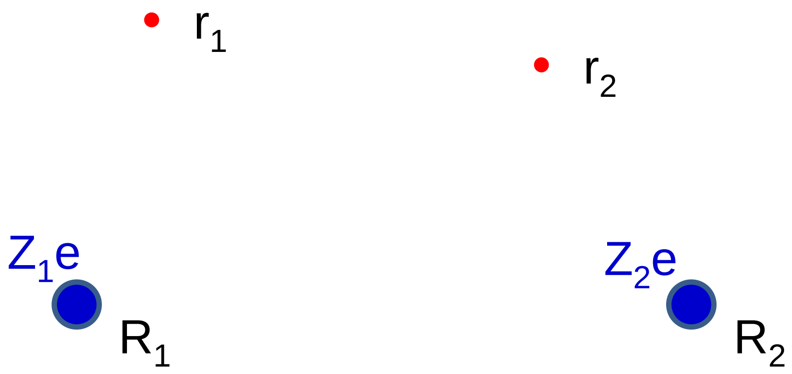
Molecules

A complete, non-relativistic, description of a system of N atoms having the positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_K, \ldots, \mathbf{R}_N)$ with n electrons located at $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_K, \ldots, \mathbf{r}_n)$ is provided by the time-dependent Schrödinger equation

$$\mathcal{H}\Xi(\mathbf{r}, \mathbf{R}; t) = i\hbar\frac{\partial}{\partial t}\Xi(\mathbf{r}, \mathbf{R}; t) \quad , \tag{1}$$

$$\mathcal{H}(\mathbf{r}, \mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r}, \mathbf{R}) + \mathcal{V}(\mathbf{r}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r}, \mathbf{R})$$



$$\underline{\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})}$$

$$\mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r},\mathbf{R}) + \mathcal{V}(\mathbf{r})$$

$$\boxed{\begin{aligned}
\mathcal{T}(\mathbf{R}) &= -\frac{\hbar^2}{2}\sum_{K=1}^{N}\frac{\boldsymbol{\nabla}_K^2}{M_K} \\
\mathcal{T}(\mathbf{r}) &= -\frac{\hbar^2}{2m_e}\sum_{k=1}^{n}\boldsymbol{\nabla}_k^2 \\
\mathcal{V}(\mathbf{R}) &= \frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N-1}\sum_{L>K}^{N}\frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \\
\mathcal{V}(\mathbf{r},\mathbf{R}) &= -\frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N}\sum_{k=1}^{n}\frac{Z_K}{|\mathbf{r}_k - \mathbf{R}_K|} \\
\mathcal{V}(\mathbf{r}) &= \frac{e^2}{4\pi\epsilon_0}\sum_{k=1}^{n-1}\sum_{l>k}^{n}\frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}
\end{aligned}}$$

$$\mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})\phi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})\phi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}\Xi(\mathbf{r},\mathbf{R};t) = i\hbar\frac{\partial}{\partial t}\Xi(\mathbf{r},\mathbf{R};t)$$

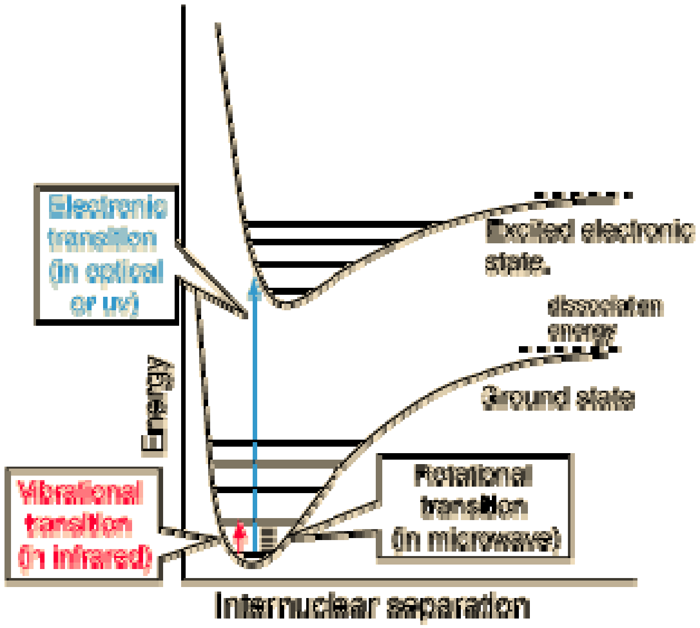
$$\left[\mathcal{T}(\mathbf{R}) + E_i(\mathbf{R})\right]\chi_i = i\hbar\frac{\partial}{\partial t}\chi_i$$

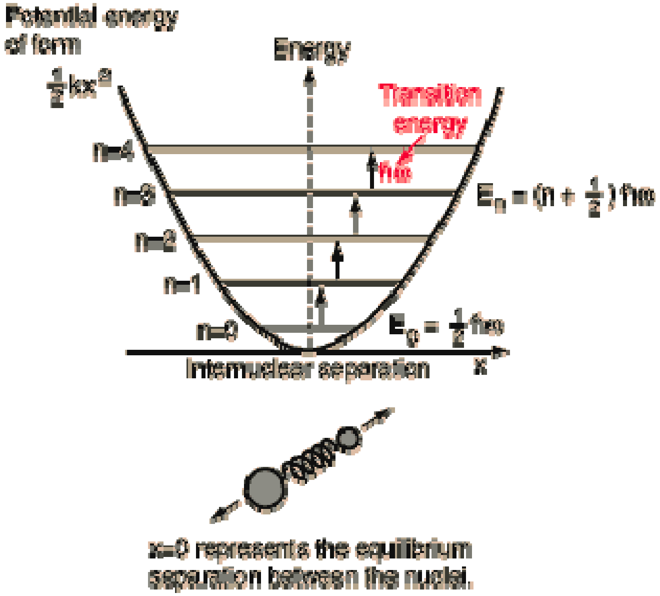
$$\Xi(\mathbf{r},\mathbf{R};t) \approx \phi_i(\mathbf{r},\mathbf{R})\chi_i(\mathbf{R},t)$$

Born-Oppenheimer Approximation

Born-Oppenheimer Approximation

$$\psi_{\text{molecule}}(\vec{r}_i,\vec{R}_j) = \psi_{\text{electrons}}(\vec{r}_i,\vec{R}_j)\psi_{\text{nuclei}}(\vec{R}_j)$$



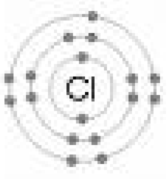


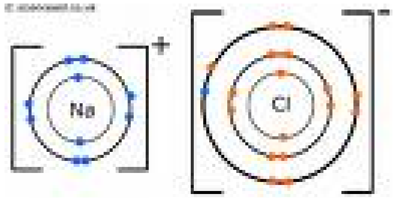
Ionic Bonds

An **ionic bond** is a type of chemical bond that involves a metal and a nonmetal ion through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions. The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

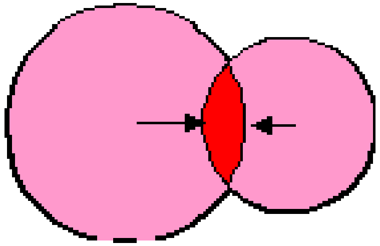
For example:

$$Na + Cl \rightarrow Na^+ + Cl^- \rightarrow NaCl$$





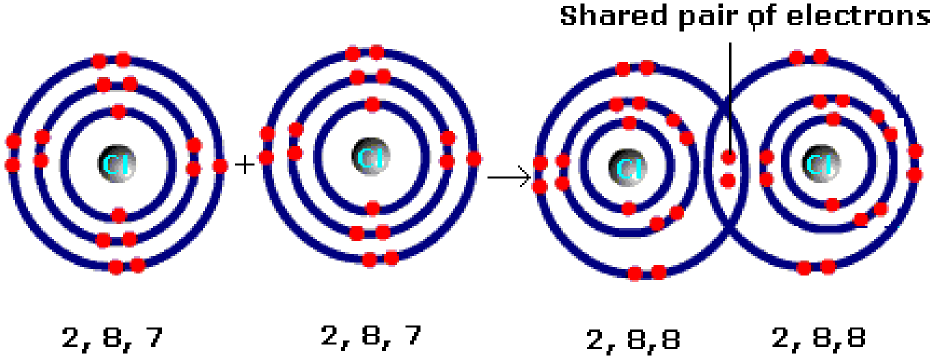
Covalent Bonds



A covalent bond is formed when the electron clouds of two atoms overlap. Where the clouds overlap they are thicker, and their electric charge is stronger.

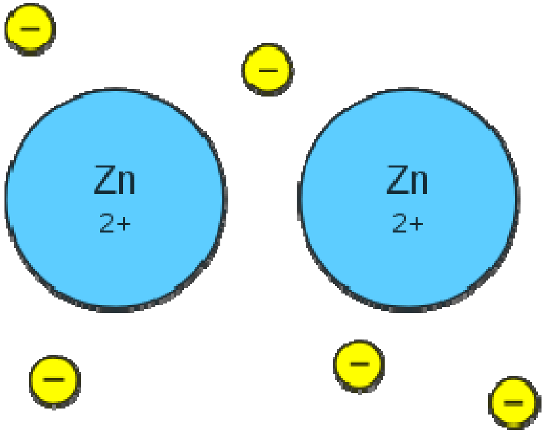
Both nuclei feel a force of attraction towards this thick electron cloud, and so the two atoms are held together.

$$Cl + Cl \longrightarrow Cl_2$$



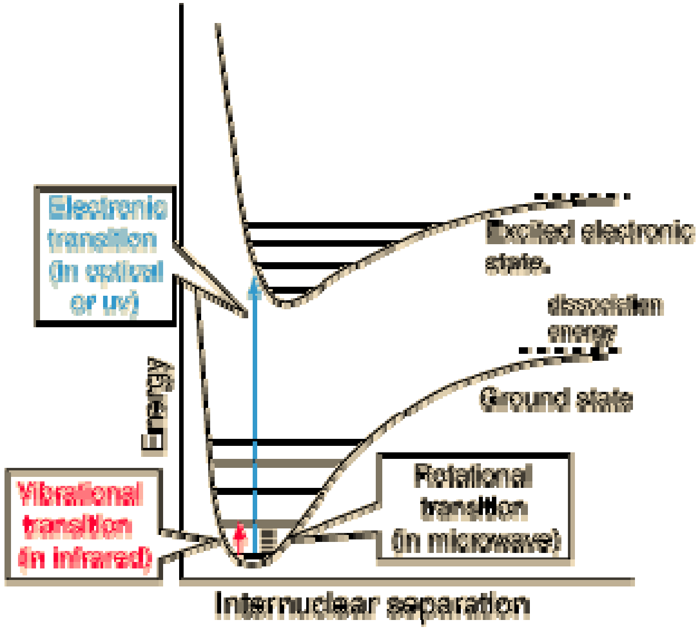
Metallic Bonds

Metallic bonding is the electromagnetic interaction between delocalized electrons, called conduction electrons and gathered in an "electron sea", and the metallic nuclei within metals. Understood as the sharing of "free" electrons among a lattice of positively-charged ions (cations; however, this simplistic view holds true for very few metals. In a more quantum-mechanical view, the conduction electrons divide their density equally over all atoms that function as neutral (non-charged) entities. Metallic bonding accounts for many physical properties of metals, such as strength, malleability, thermal and electrical conductivity, opacity, and luster.



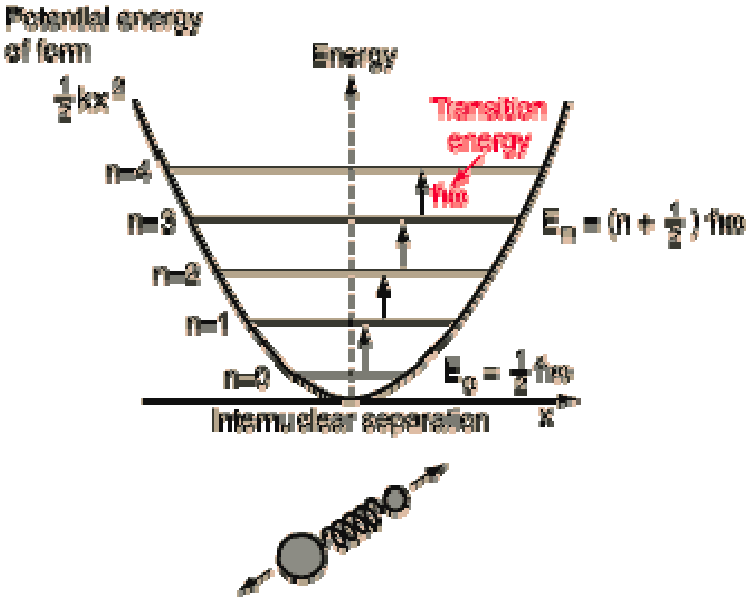
Electronic Spectroscopy

1. Photons in, photons out – PL
2. Photons in, electrons out – UPS, XPS
3. Electrons in, electrons out – EELS

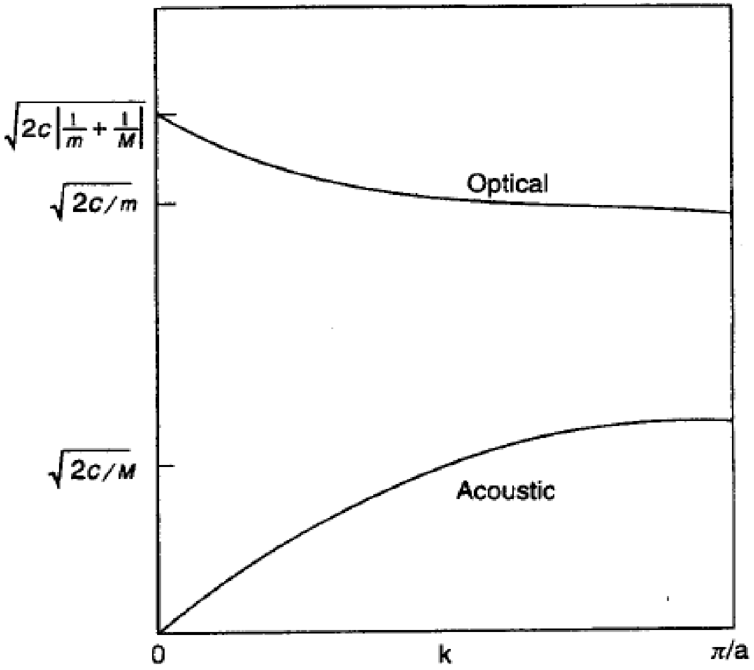


Vibrational Spectroscopy

1. Photons in, photons out – IR, Raman
2. Electrons in, electrons out – EELS



x=0 represents the equilibrium separation between the nuclei.



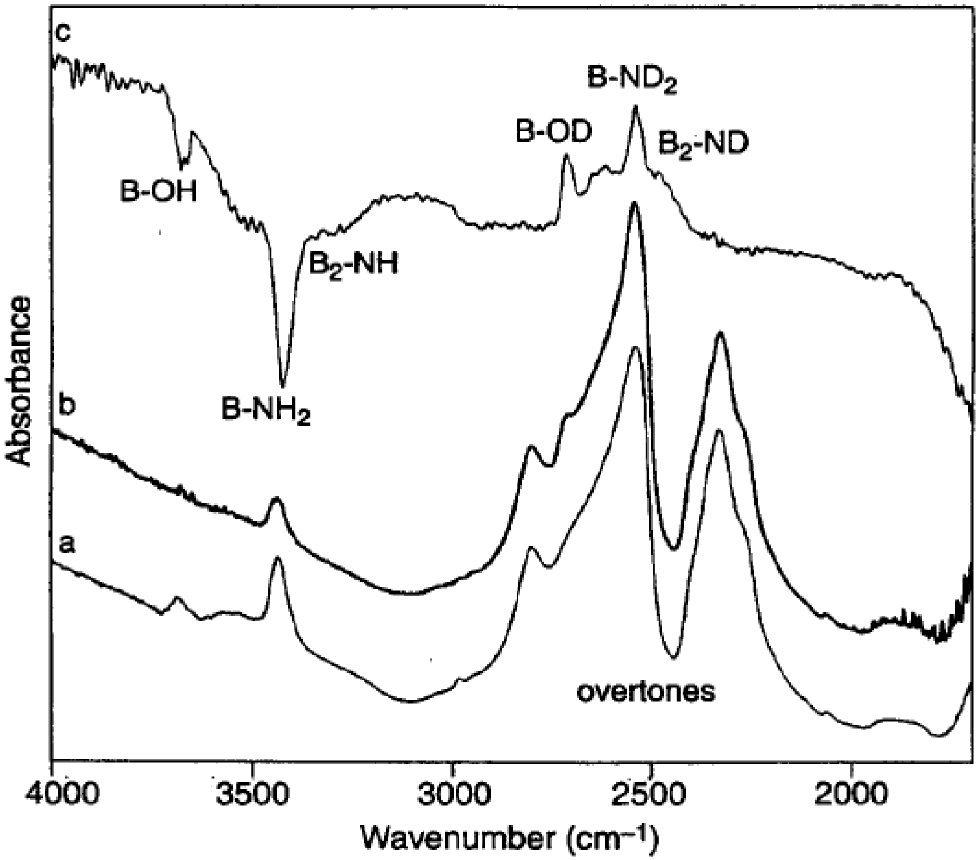
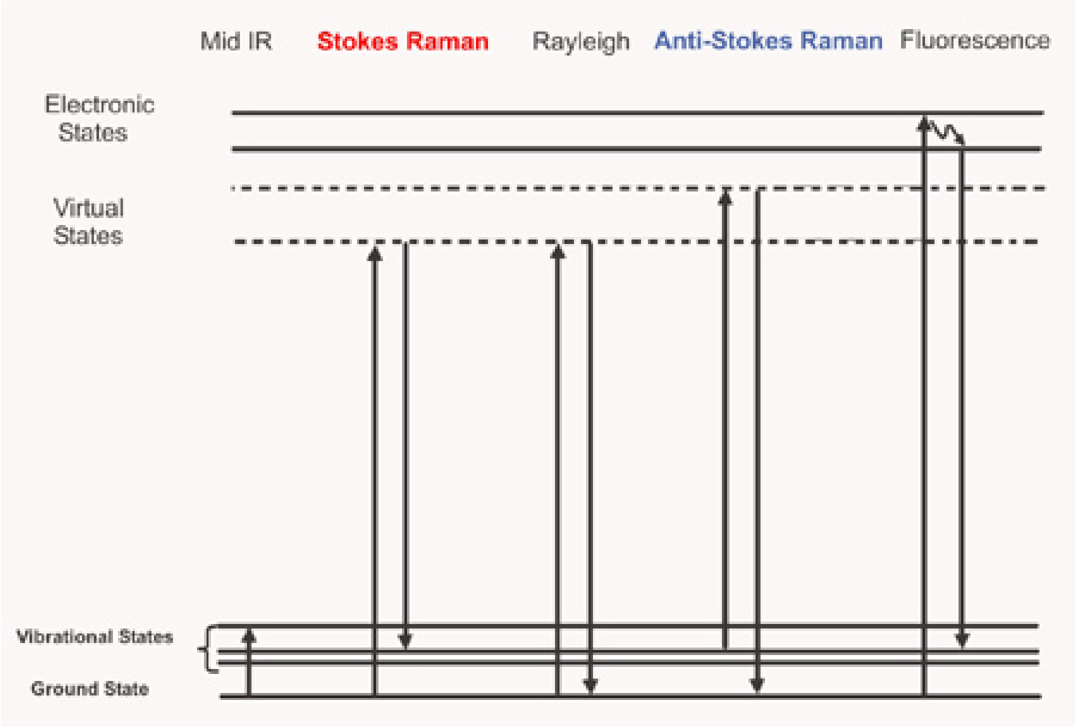
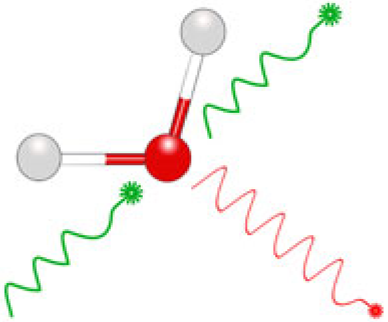
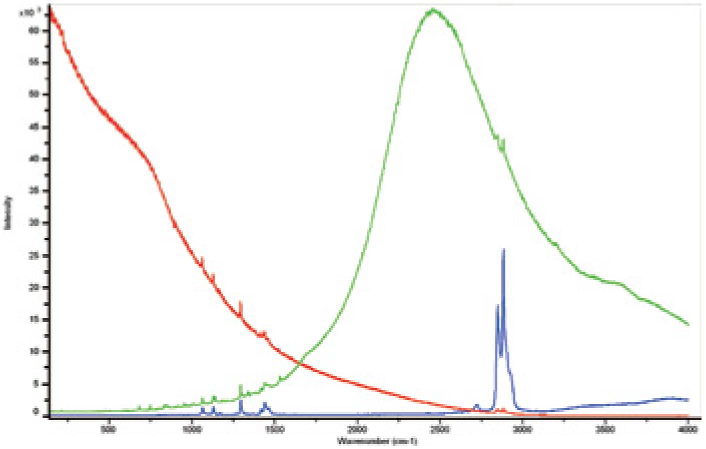


Figure 8.5. FTIR spectra of boron nitride nanopowder surfaces after activation at 875 K (tracing a), after subsequent deuteration (tracing b), and (c) difference spectrum of *a* subtracted from *b* (tracing c). [From M.-I. Baraton and L. Merhari, P. Quintard, V. Lorezenvilli, *Langmuir*, **9**, 1486 (1993).]

The Theory of Raman Spectroscopy







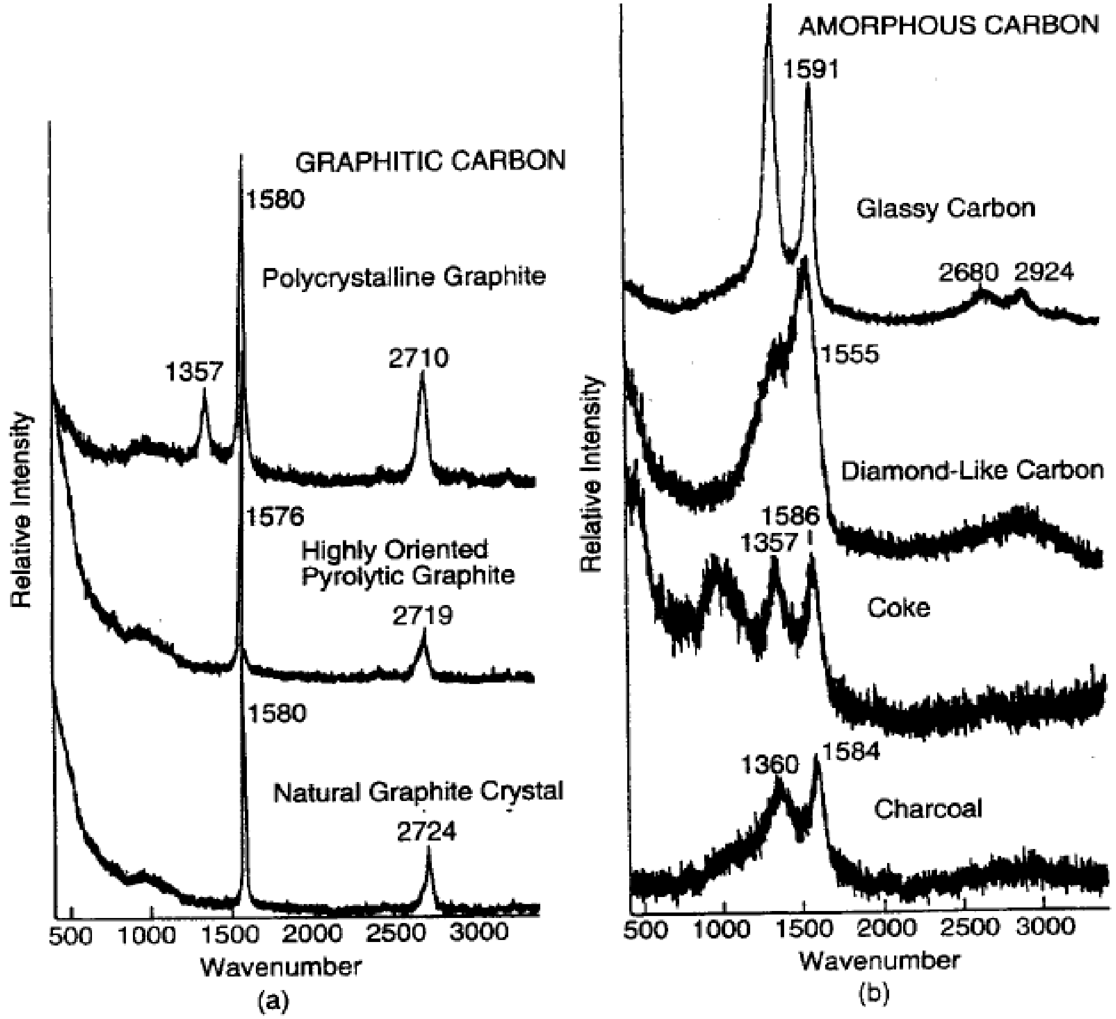
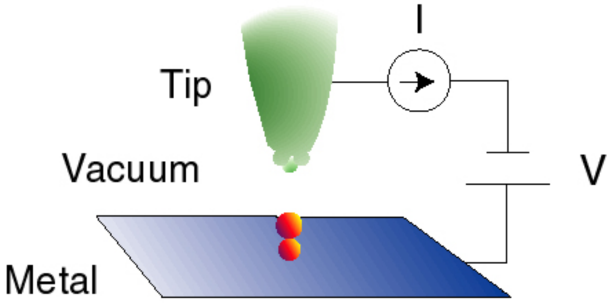
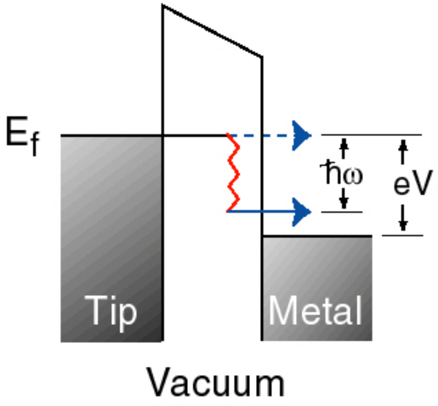


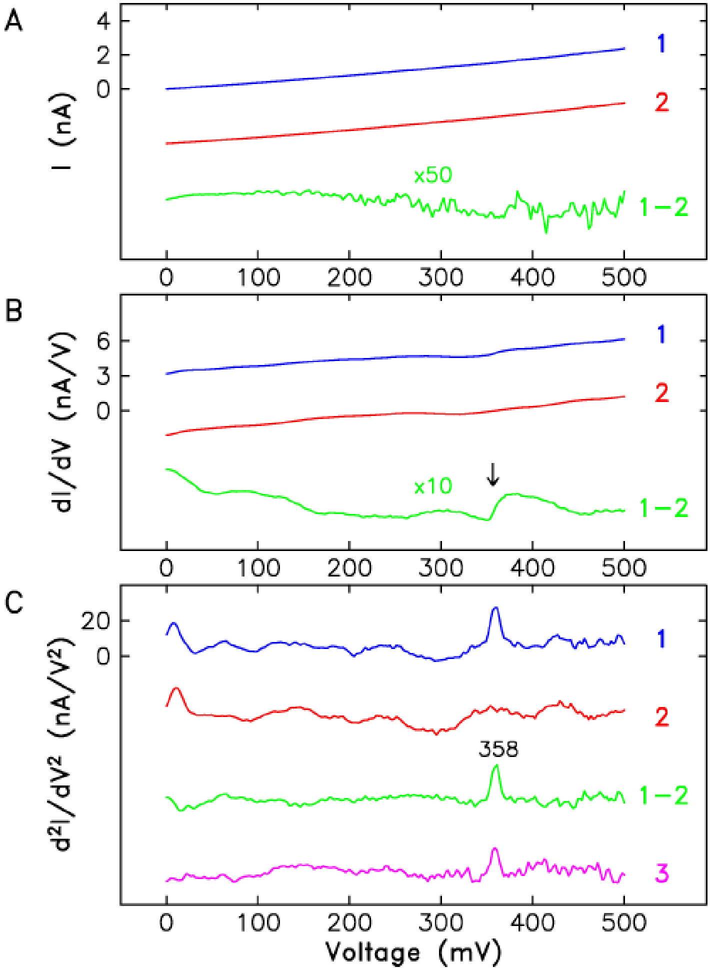
Figure 8.19. Raman spectra of (a) crystalline graphites and (b) noncrystalline, mainly graphitic, carbons. The *D* band appears near 1355 cm^{-1} and the *G* band, near 1580 cm^{-1}. [From D. S. Knight and W. B. White, *J. Mater, Sci.* **4**, 385 (1989).]

Inelastic Tunneling

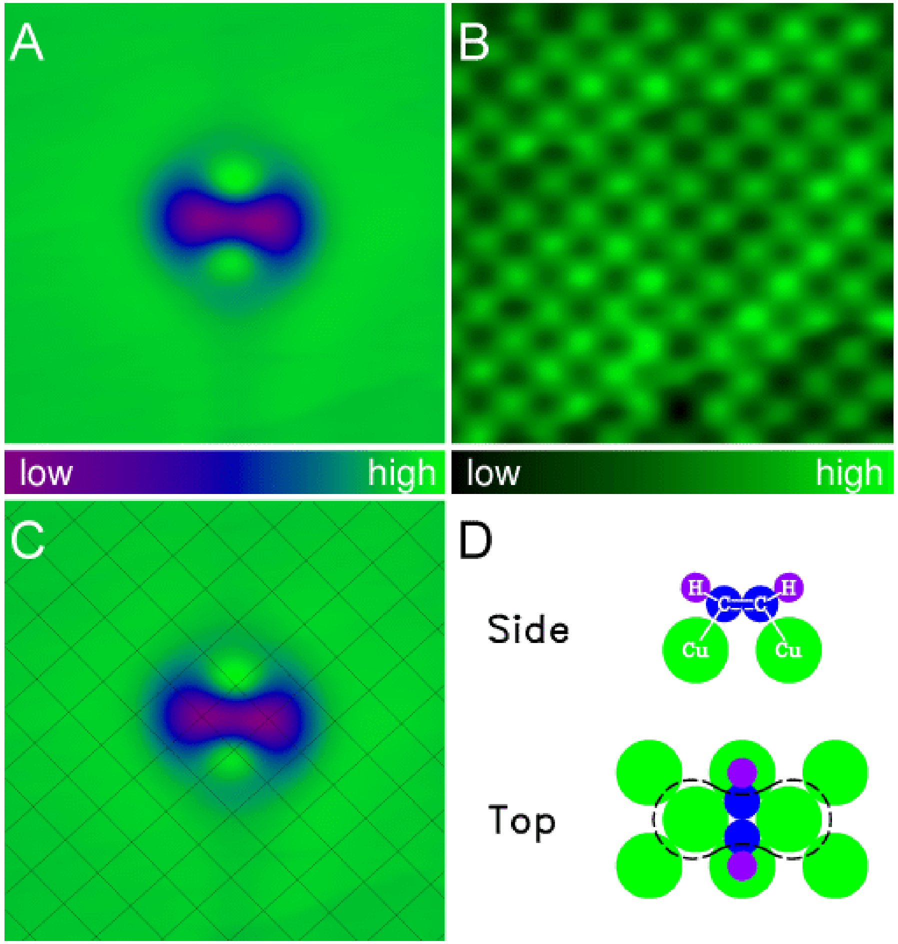
Elastic vs. Inelastic Tunneling

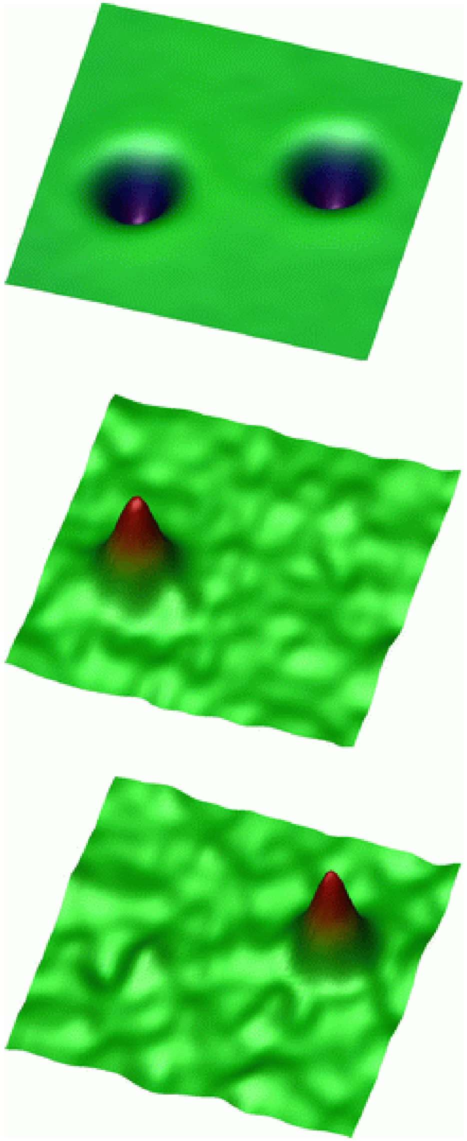






Single Molecule Vibrational Spectroscopy and Microscopy





B.C. Stipe, M.A. Rezaei, and W. Ho,
Science **280**, 1732-1735 (1998).

Homework#4 (Nov. 2, 2009):

The first ionization potential for K is 4.3 eV; the ion Br^- is lower in energy by 3.5 eV than the neutral Br atom. Compute the largest separation of K^+ and Br^- ions that gives a bound KBr molecule.