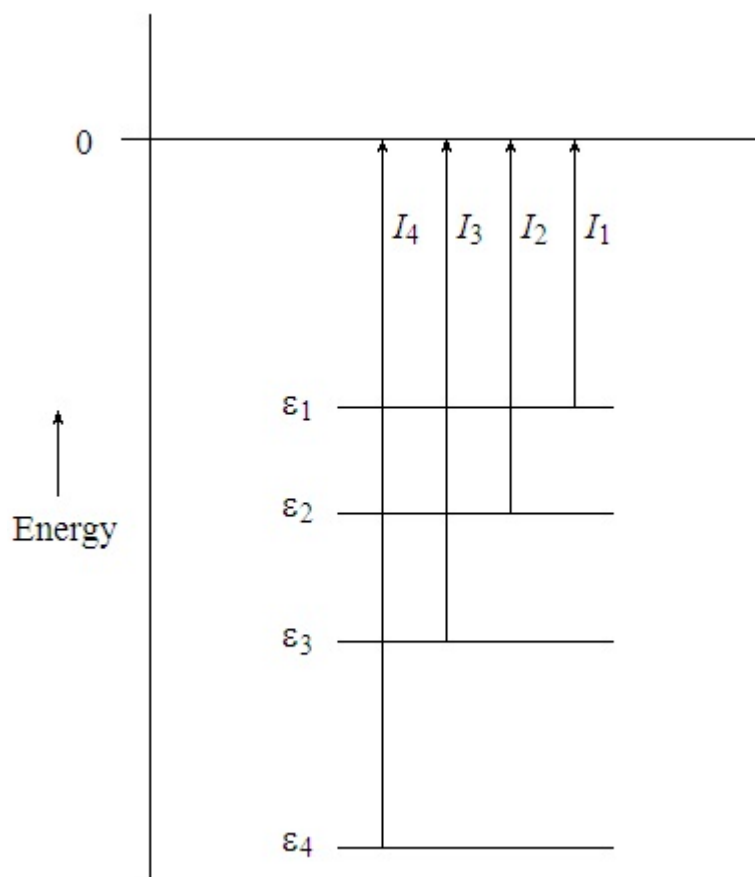
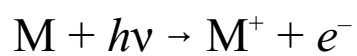


Ionizations from a Set of Orbitals



Koopman's theorem: Each ionization energy, I_j , is equal in magnitude to an orbital energy,

$$I_j = -\epsilon_j.$$

Photoelectric Effect

Einstein photoelectric equation:

$$E_{\text{photon}} = h\nu = I + KE$$

E_{photon} = energy of incident radiation

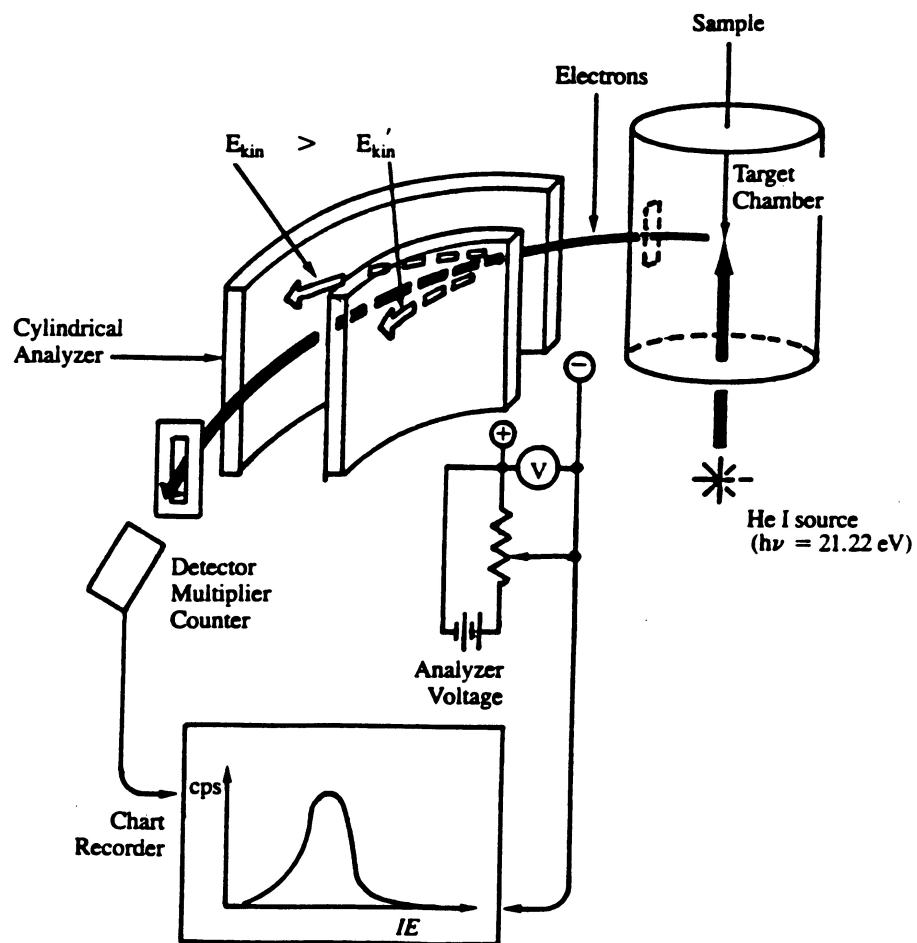
h = Planck's constant

ν = frequency of incident radiation

I = ionization energy

KE = kinetic energy of ejected electron

Ultraviolet Photoelectron Spectrometer



Ultraviolet Photoelectron Spectroscopy (P.E.S.)

P. E. S. ionization from atoms:

$$KE_j = h\nu - I_j$$

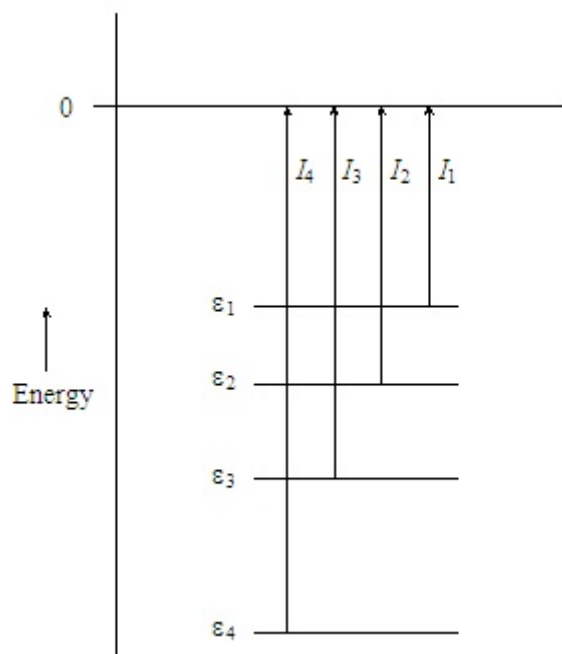
- Incident radiation: He(I) 58.4 nm = 21.22 eV.
- Only valence shell electrons removed.
- Instrument separates electrons according to kinetic energy and records numbers of electrons at each value, displayed as peaks of proportional height.

- From detected kinetic energies, ionization energies are given by

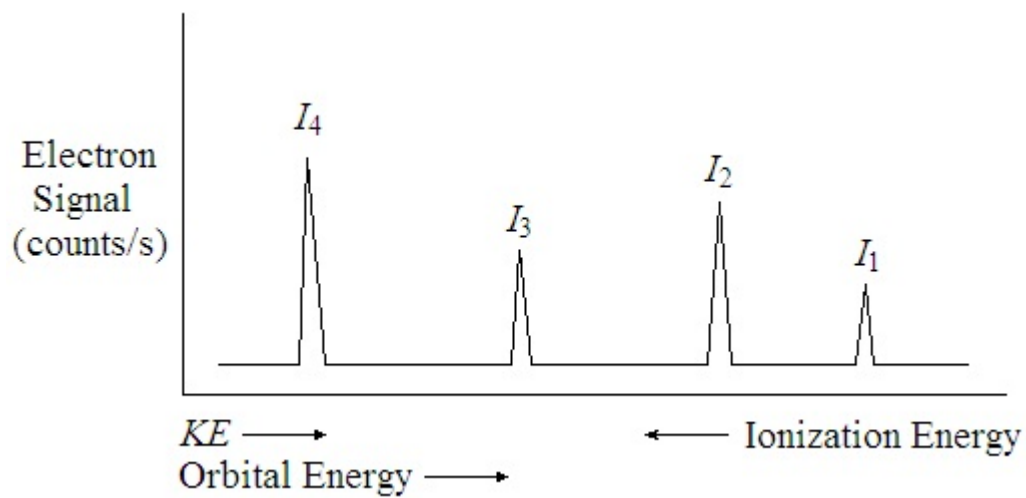
$$I_j = h\nu - KE_j$$

- Spectrum is usually displayed as electron signal (photoelectron current) vs. ionization energy.
- Intensities of peaks are proportional to the relative probabilities of photoionizations to different states of the positive ion (*relative partial ionization cross-section*).

Model Atomic P. E. S. Spectrum



Schematic P.E.S. Spectrum



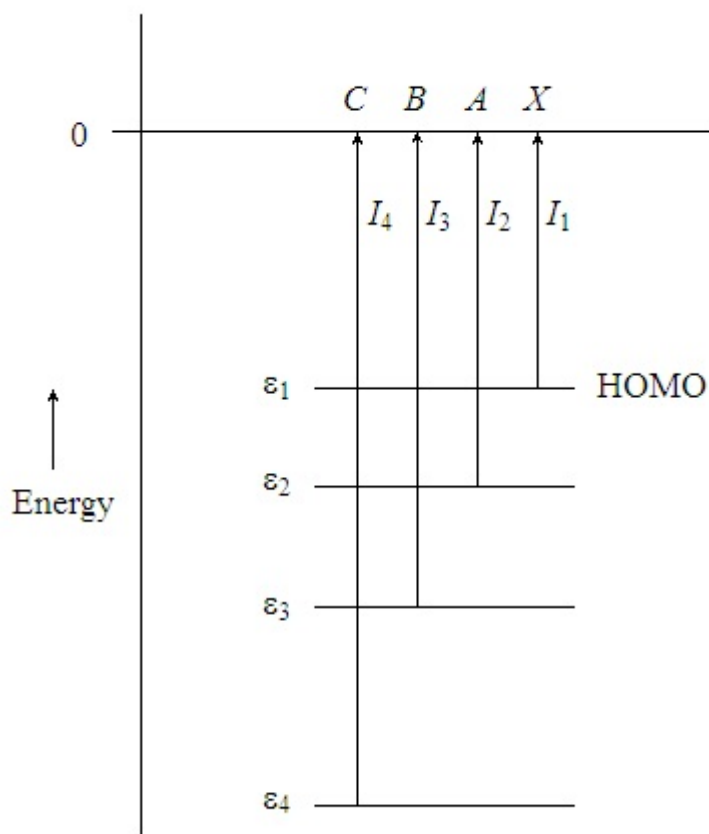
P. E. S. of Molecules

$$KE = h\nu - I - E_{\text{vib, rot}}$$

- Spectrum consists of *bands*, corresponding to ionizations from individual orbitals.
- Bands may have a single *peak* or consist of a series peaks (*fine structure*), arising from excitations to the various vibrational-rotational states of the ion, M^+ . (Usually, only vibrational fine structure is resolved.)
- Spin-orbital coupling (producing two distinct J values and corresponding energies) or Jahn-Teller effects (causing splitting of degenerate states) can cause additional band splitting.

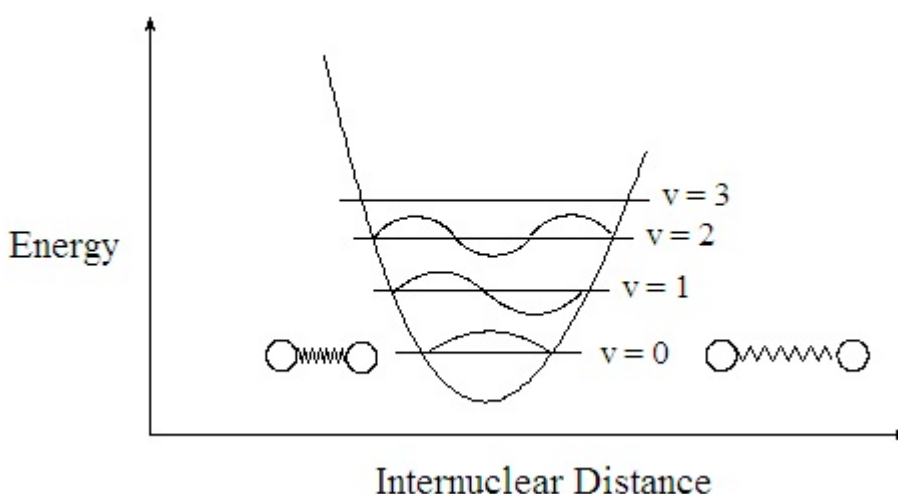
Electronic States of the Ion, M^+

- ☞ The electronic state of the ion M^+ depends upon the orbital of the neutral molecule from which the electron is ejected.
- The lowest energy state (ground-state) of M^+ (designated X) is produced by ejecting an electron from the highest-occupied M.O. of the neutral molecule (HOMO).
 - » The ionization energy to produce X is the lowest of the series and corresponds to I_1 .
 - Higher-energy states of M^+ (designated A, B, C, \dots) are produced by ejecting an electron from lower-energy M.O.'s.
 - » Ionizations producing A, B, C, \dots are I_2, I_3, I_4, \dots



Vibrational States of M and M⁺

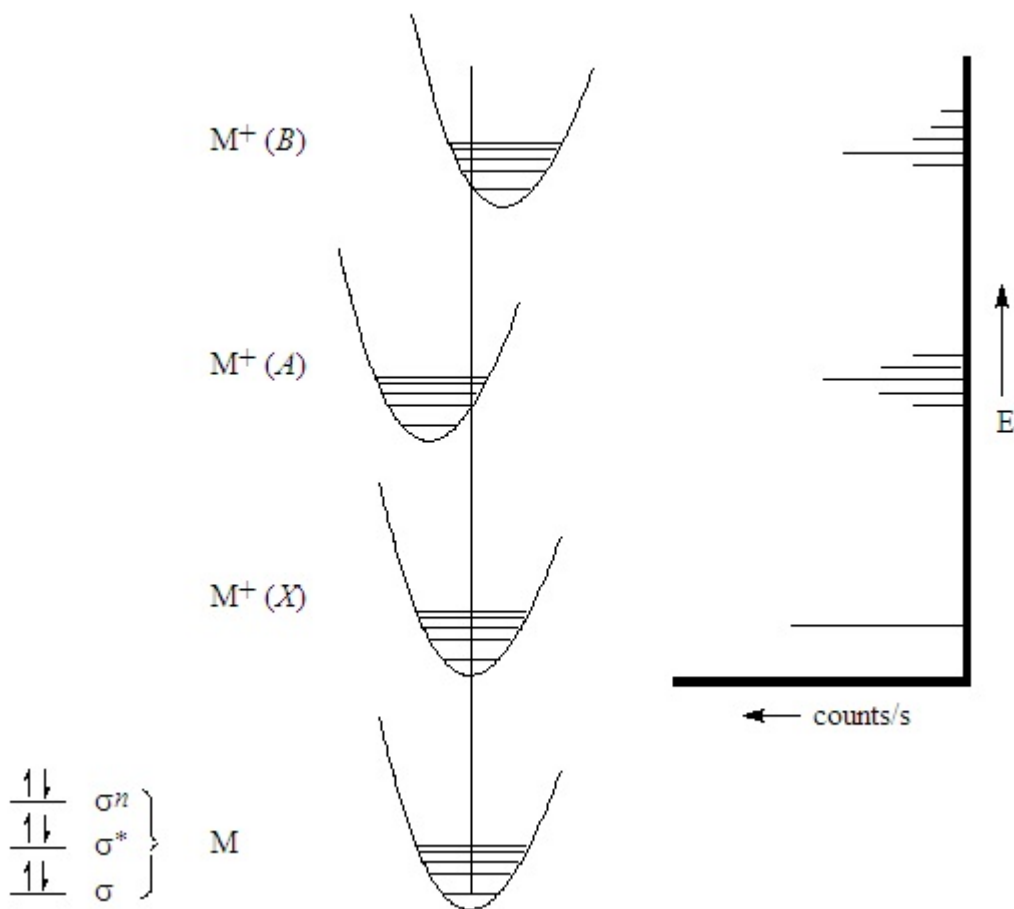
- Both M and M⁺ may be in any allowed vibrational state, corresponding to the vibrational quantum numbers $v = 0, 1, 2, \dots$ and $v' = 0, 1, 2, \dots$, respectively
 - » The frequency, ν or ν' , does not change with v or v' .
 - » Vibrational amplitude increases with v .



- At room temperature, most M molecules are in their vibrational ground state, $v = 0$.
- Ionization to M⁺ can result in an ion in any of its possible electronic states, each of which may be in any of their allowed vibrational states, v' .

Ionizations as State-to-State Transitions

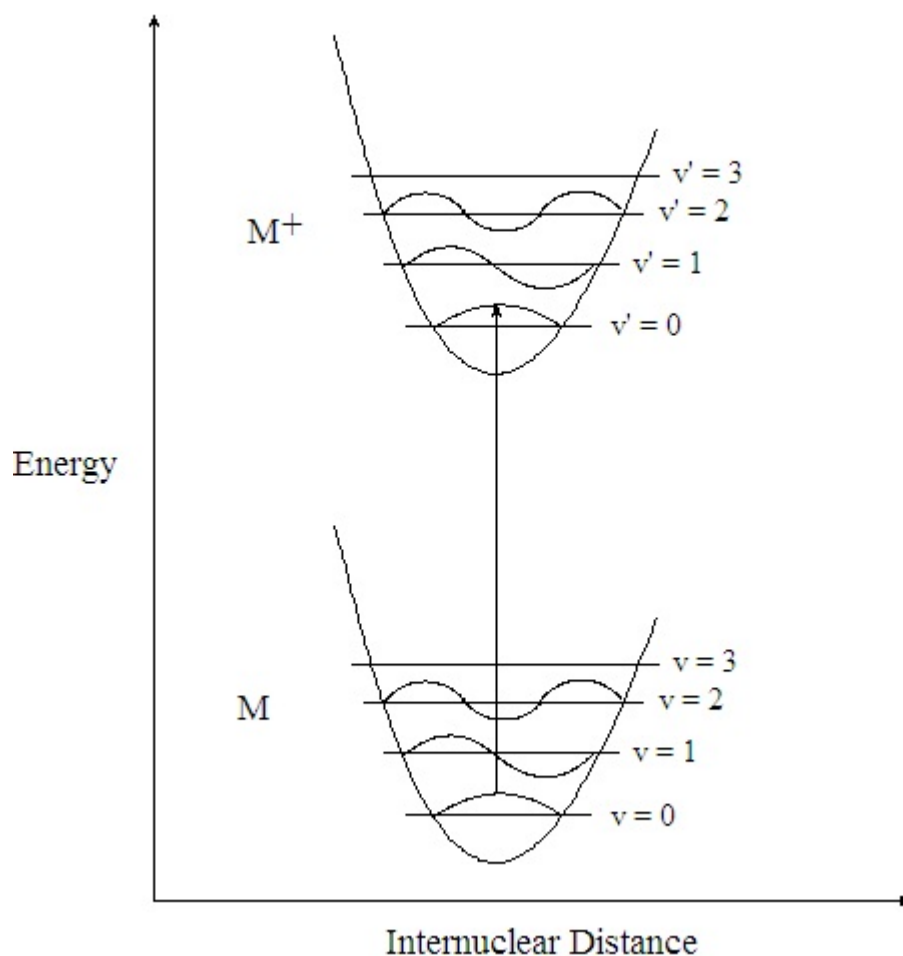
- ☞ Possible ionizations may be viewed as state-to-state transitions.
- Adiabatic Transition - Transition from M in $v = 0$ to M^+ in $v' = 0$.
 - Vertical Transition - Transition without change in bond length (*Franck-Condon Principle*).



Peak Intensities and Band Patterns

- ☞ The most intense peak (most probable transition) for a given ionization corresponds to the vertical transition to the vibrational level for which there is maximum overlap between the vibrational wave functions for the ground- and excited-state energy levels.
- The $v = 0$ state of M has maximum wave-function amplitude at the center of the bond, so a vertical transition always occurs from that position.
 - If bond strength is unaffected by ionization, the strongest peak will correspond to $M (v = 0) \rightarrow M^+ (v' = 0)$; i.e., the adiabatic transition.
 - If bond strength is changed by ionization, the strongest peak (vertical transition) will correspond to $M (v = 0) \rightarrow M^+ (v' > 0)$.
 - Transitions to other v' states (non-vertical transitions) will have lesser intensities, varying according to their probabilities (*Franck-Condon distribution*).

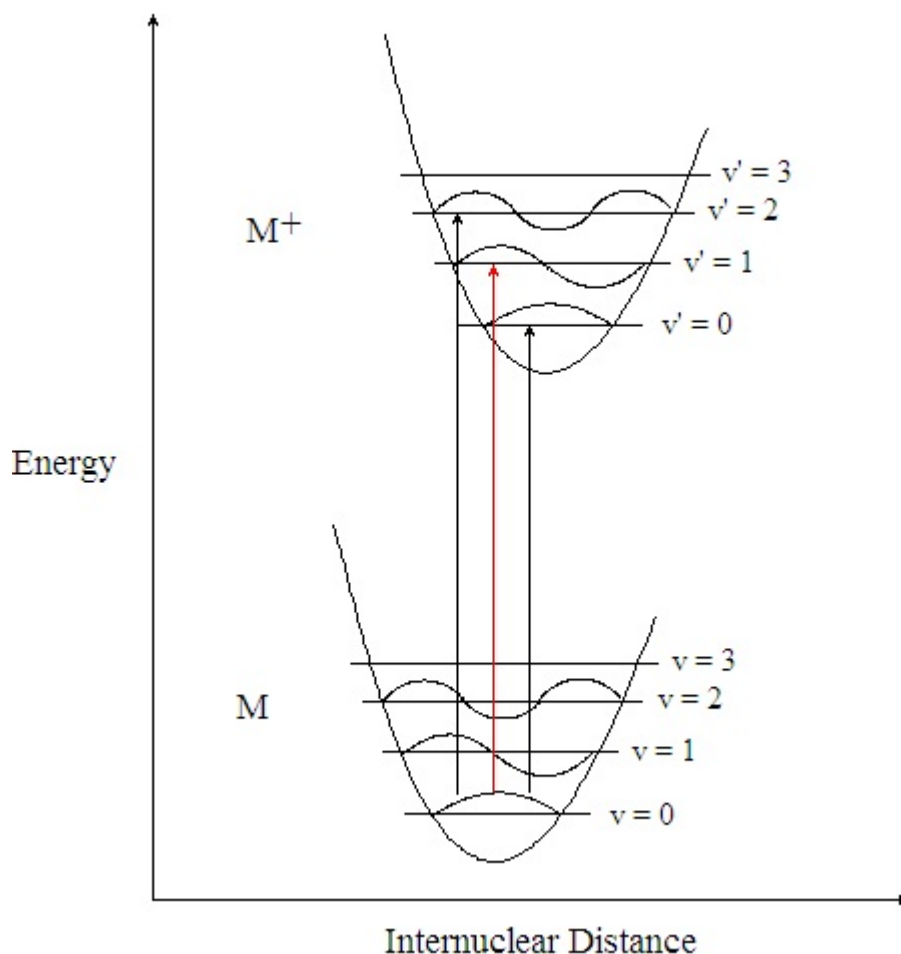
Molecular Ionization from a Non-Bonding MO



- Ionization from a non-bonding M.O. does not change bond length, so the vertical transition is the adiabatic transition, $M(v = 0) \rightarrow M^+(v' = 0)$.
- Transitions to other v' states (other Franck-Condon transitions) have much less probability, due to the poor overlap between $\Psi(v = 0)$ and $\Psi'(v' > 0)$.

☞ P.E.S. bands for ionizations from non-bonding M.O.s tend to have little or no vibrational fine structure.

Molecular Ionization from a Bonding MO

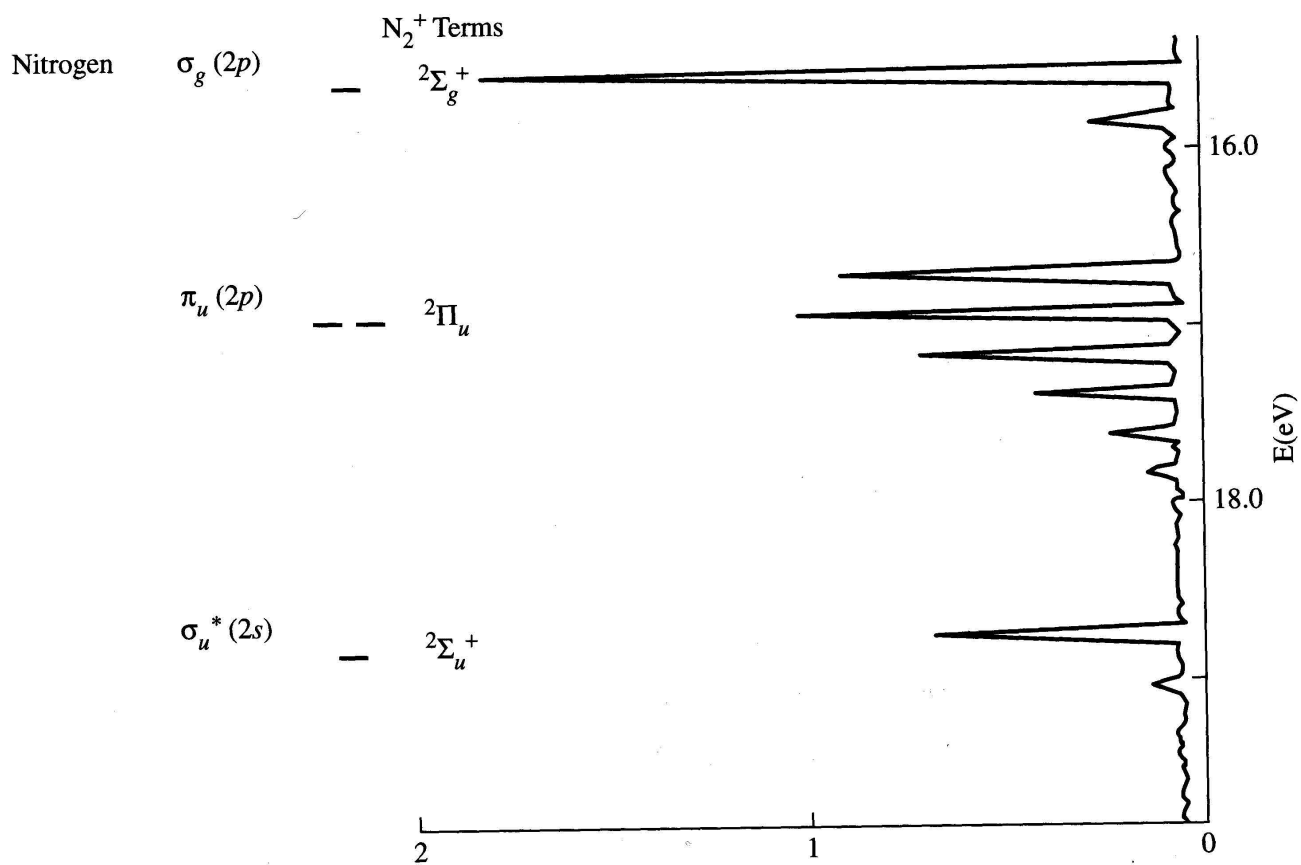


- Ionization from a bonding or anti-bonding M.O. causes a change in bond length in the ion M^+ , compared to the bond length in M.
- The vertical transition is to an M^+ vibrational state $v' > 0$ with maximum wave-function overlap at the same inter-nuclear separation as the normal bond length of the neutral molecule, M. (*Not* the adiabatic transition).
- Transitions to other v' states are possible with lesser probability, resulting in vibrational fine structure on the ionization band.

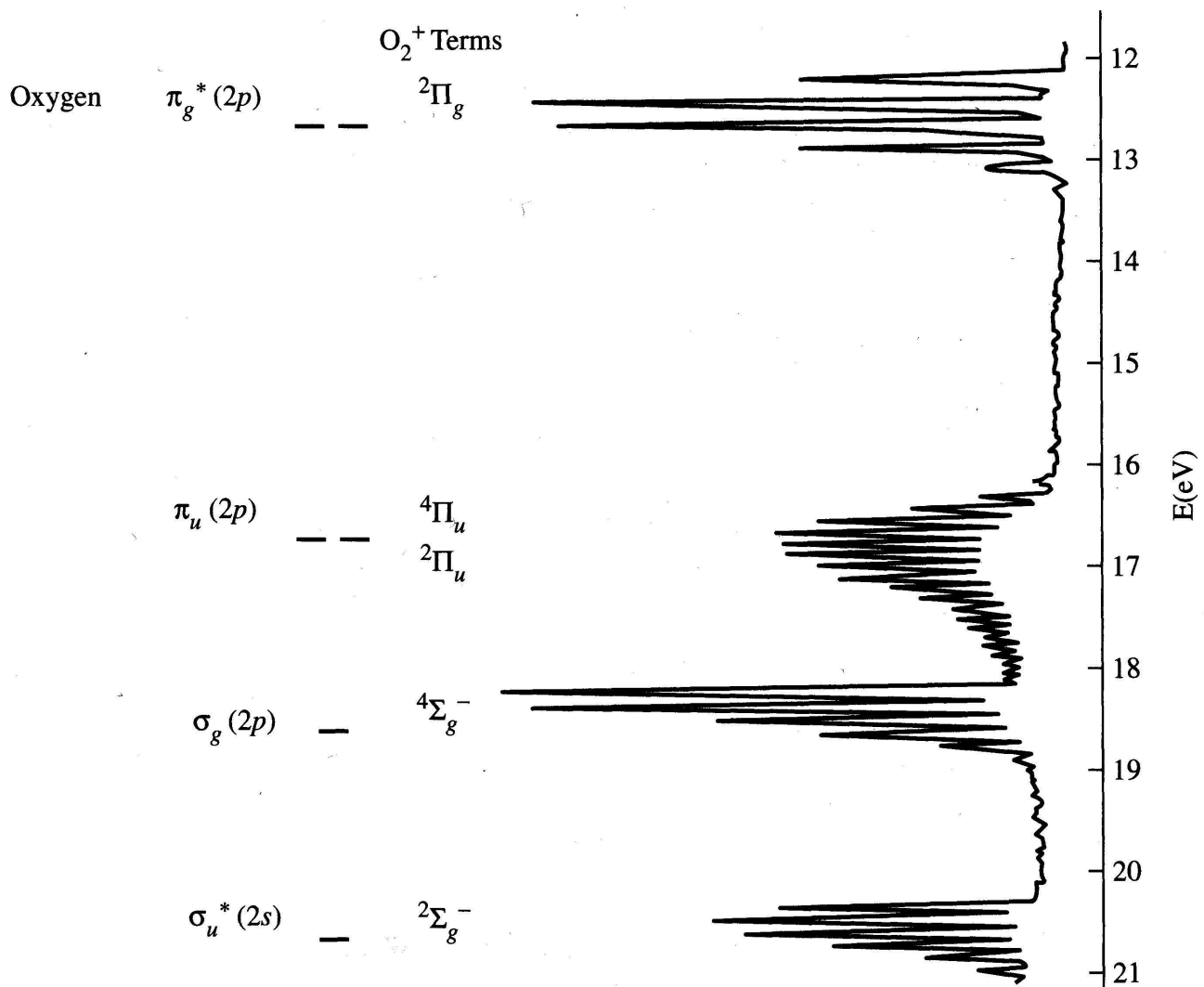
Molecular Ionization from a Bonding MO - Cont.

- The frequency separations between the vibrational peaks can be used to calculate the vibrational frequency of the ion, M^+ .
- ☞ P.E.S. bands for ionizations from bonding or antibonding M.O.s tend to have pronounced vibrational fine structure.

PES of N₂



PES of O₂



PES of CO

