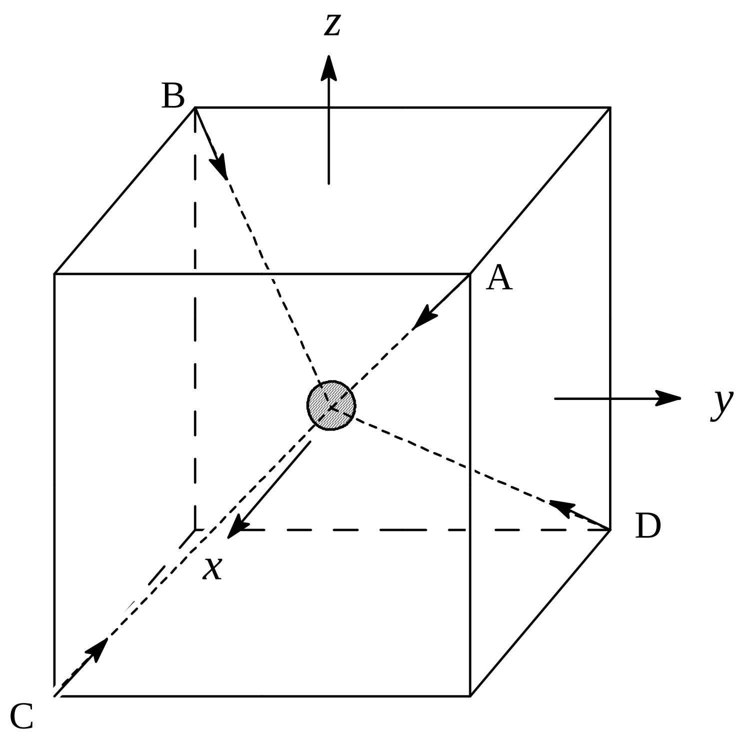
General MOs for CH_4

- ✔ The four pendant H atoms in their sigma interactions with central C AOs can be represented by a set of four tetrahedrally oriented vectors point toward the center of a cube.



- ✔ Counting nonshifted vectors after applying a representative operation from each class yields the following reducible representation:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{SALC}	4	1	0	0	2

$$\Rightarrow A_1 + T_2$$

Forming the Hydrogen SALCs

- ✔ The following SALC equations have the requisite symmetries:

$$A_1: \quad \Phi_1 = ½\{1s_\mathrm{A} + 1s_\mathrm{B} + 1s_\mathrm{C} + 1s_\mathrm{D}\}$$

$$\begin{aligned} T_2: \quad \Phi_2 &= ½\{1s_\mathrm{A} + 1s_\mathrm{B} - 1s_\mathrm{C} - 1s_\mathrm{D}\} \\ \Phi_3 &= ½\{1s_\mathrm{A} - 1s_\mathrm{B} - 1s_\mathrm{C} + 1s_\mathrm{D}\} \\ \Phi_4 &= ½\{1s_\mathrm{A} - 1s_\mathrm{B} + 1s_\mathrm{C} - 1s_\mathrm{D}\} \end{aligned}$$

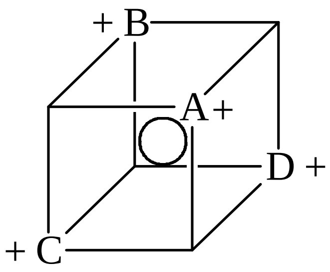
Carbon AO Symmetries

- ✔ From vector transformation properties listed in the T_d character table:

$$s = A_1 \qquad (p_x, p_y, p_z) = T_2$$

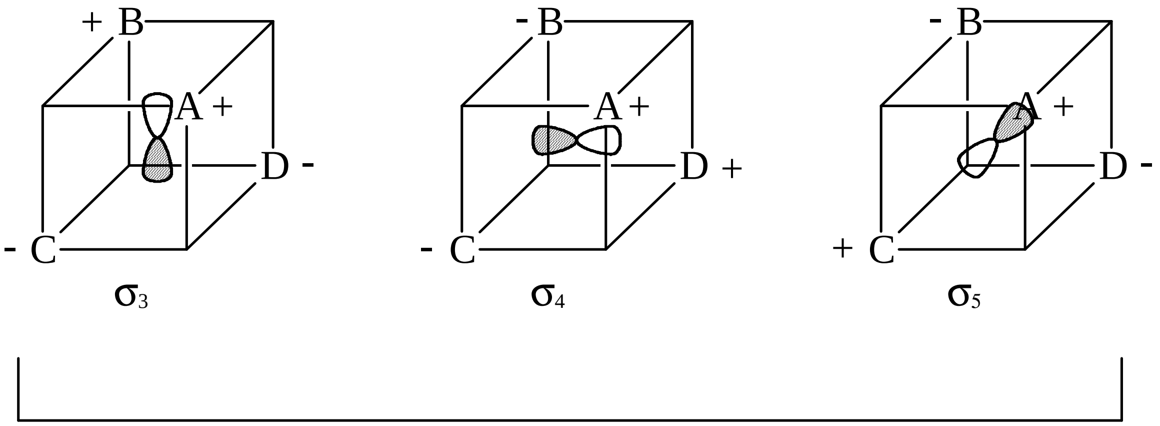
- ✔ Assuming 1*s* orbital on C is nonbonding, LCAOs are formed between 2*s* and 2*p* AOs on C with the four SALCs defined above.

Representations of Bonding LCAO-MOs of CH_4



σ_2

A_1



σ_3 σ_4 σ_5

T_2

LCAO MO Equations for CH_4

$\sigma_1^{n} = c_0(1s)$ nonbonding core (a_1)

a_1 MOs:

$\sigma_2 = c_1(2s) + c_2\Phi_1$ bonding
$\sigma_6^{*} = c_3(2s) - c_4\Phi_1$ antibonding

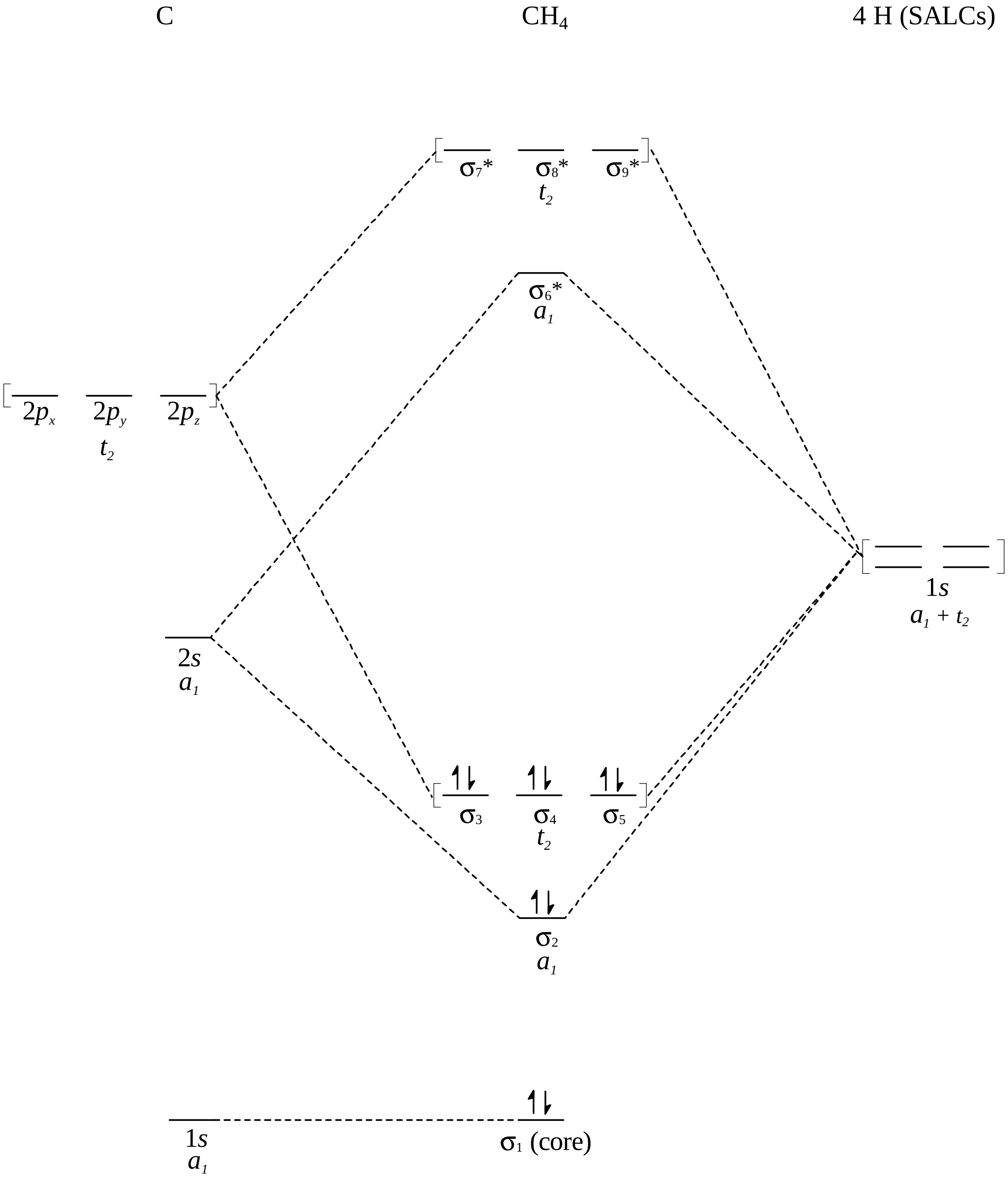
t_2 MOs:

$\sigma_3 = c_5(2p_z) + c_6\Phi_2$ bonding
$\sigma_7^{*} = c_7(2p_z) - c_8\Phi_2$ antibonding

$\sigma_4 = c_9(2p_y) + c_{10}\Phi_3$ bonding
$\sigma_8^{*} = c_{11}(2p_y) - c_{12}\Phi_3$ antibonding

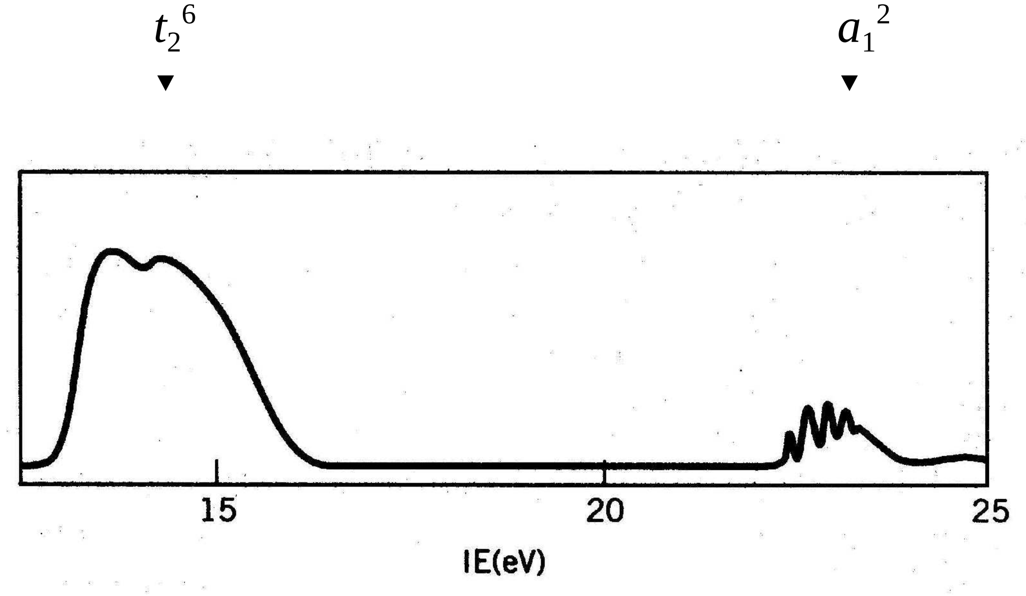
$\sigma_5 = c_{13}(2p_x) + c_{14}\Phi_4$ bonding
$\sigma_9^{*} = c_{15}(2p_x) - c_{16}\Phi_2$ antibonding

Qualitative MO Scheme for CH_4



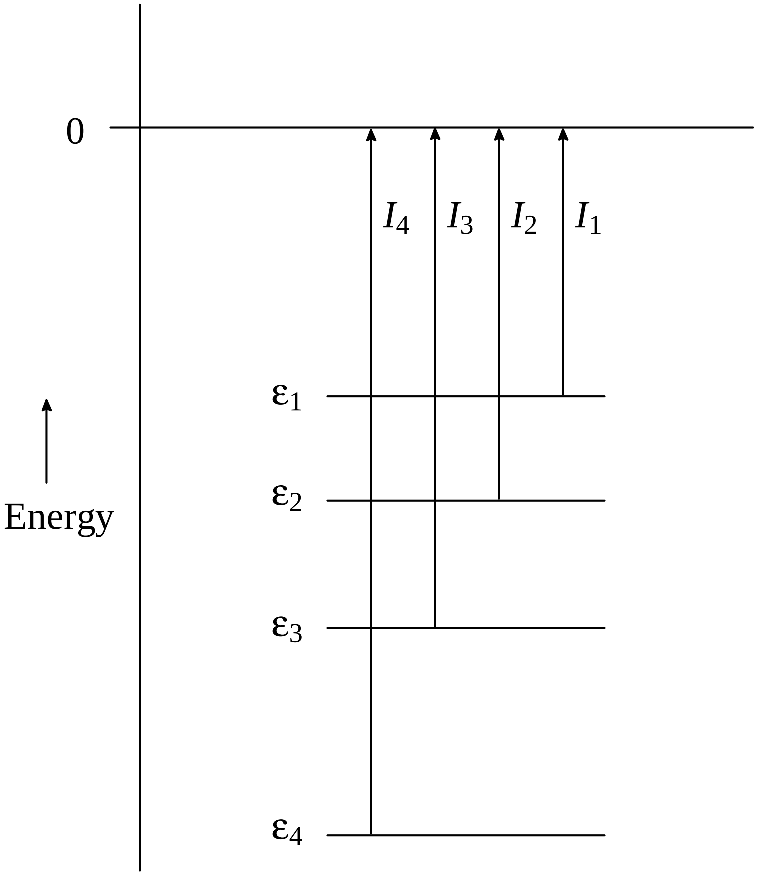
Photoelectron Spectrum of CH_4

✔ Photoelectron spectroscopy (P.E.S.) gives experimental measurement of orbital energies.



Ionizations from a Set of Orbitals

$$\mathrm{M} + h\nu \rightarrow \mathrm{M}^{+} + e^{-}$$



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

$$I_j = -\varepsilon_j.$$

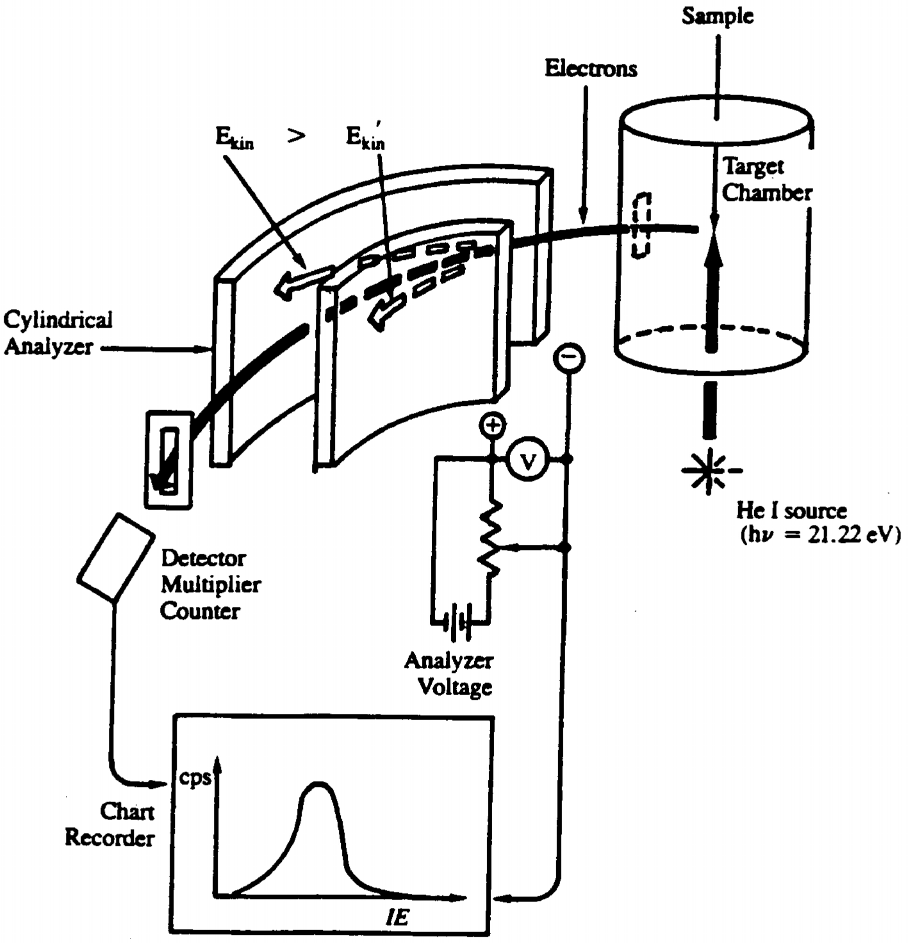
Photoelectric Effect

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:

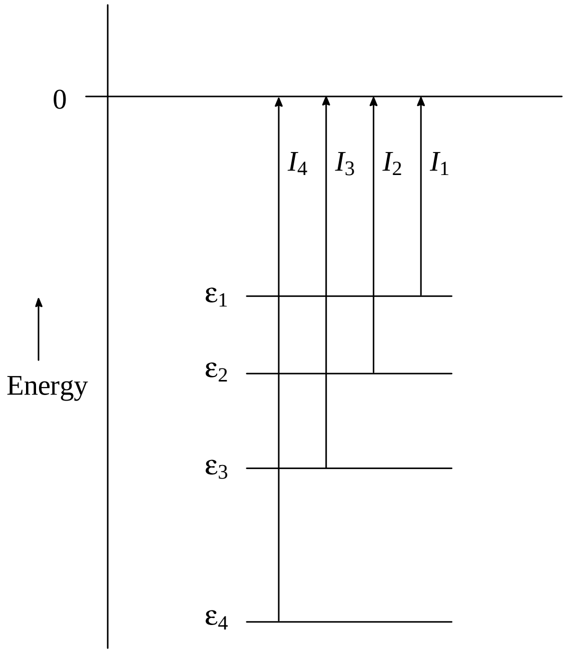
$$KE_j = h\nu - I_j$$

- 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

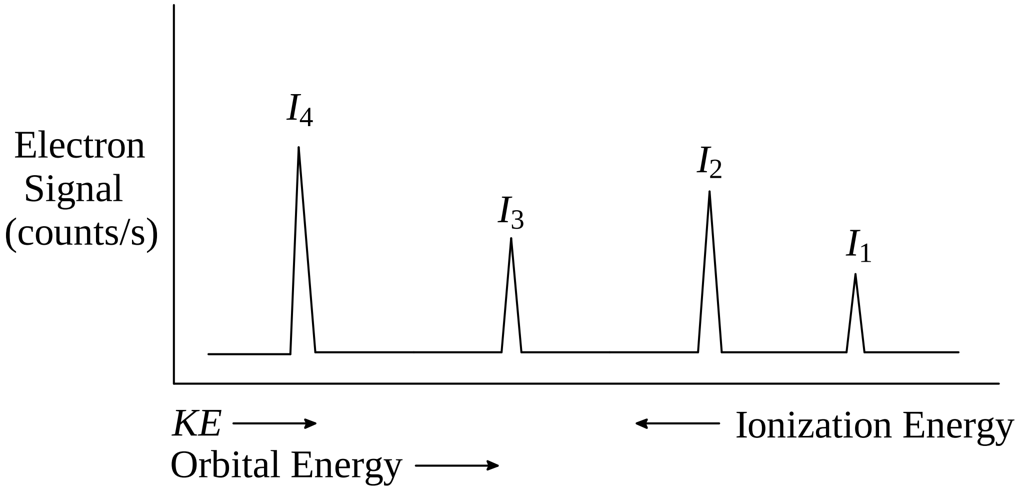
$$I_j = h\nu - KE_j$$

- 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.

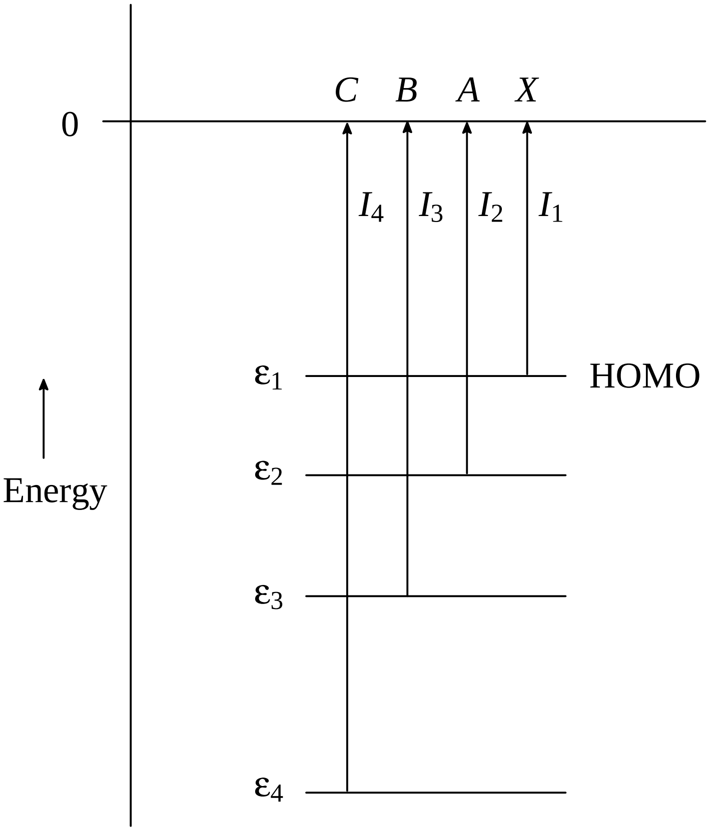
- Bands may have a single *peak* or consist of a series peaks (*fine structure*), arising from excitations to the various vibrational-rotational states of the ion, M^+. (Usually, only vibrational fine structure is resolved.)

- 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^+

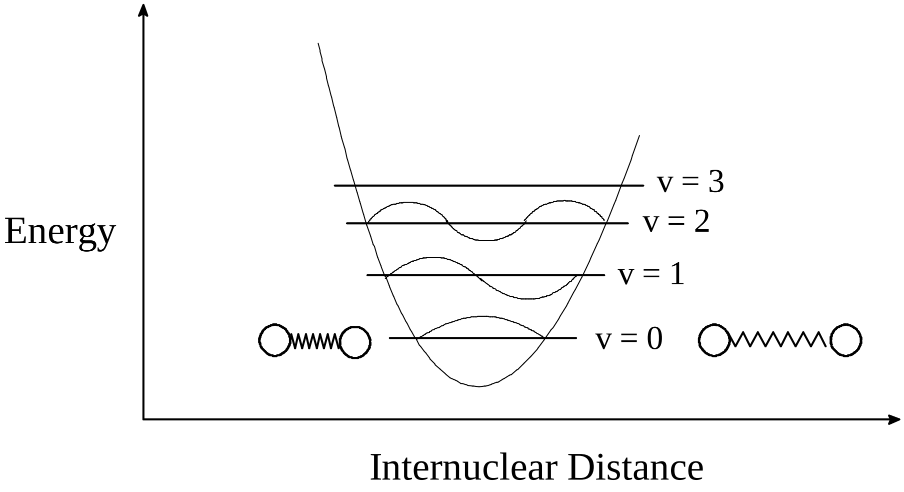
☞ The electronic state of the ion M^+ depends upon the orbital of the neutral molecule from which the electron is ejected.

- 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*, ...) are produced by ejecting an electron from lower-energy M.O.'s.
  - » Ionizations producing *A*, *B*, *C*, ... are I_2, I_3, I_4, ...



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, ... and v' = 0, 1, 2, ..., respectively
    - » The frequency, ν or ν', does not change with v or v'.
    - » Vibrational amplitude increases with v.



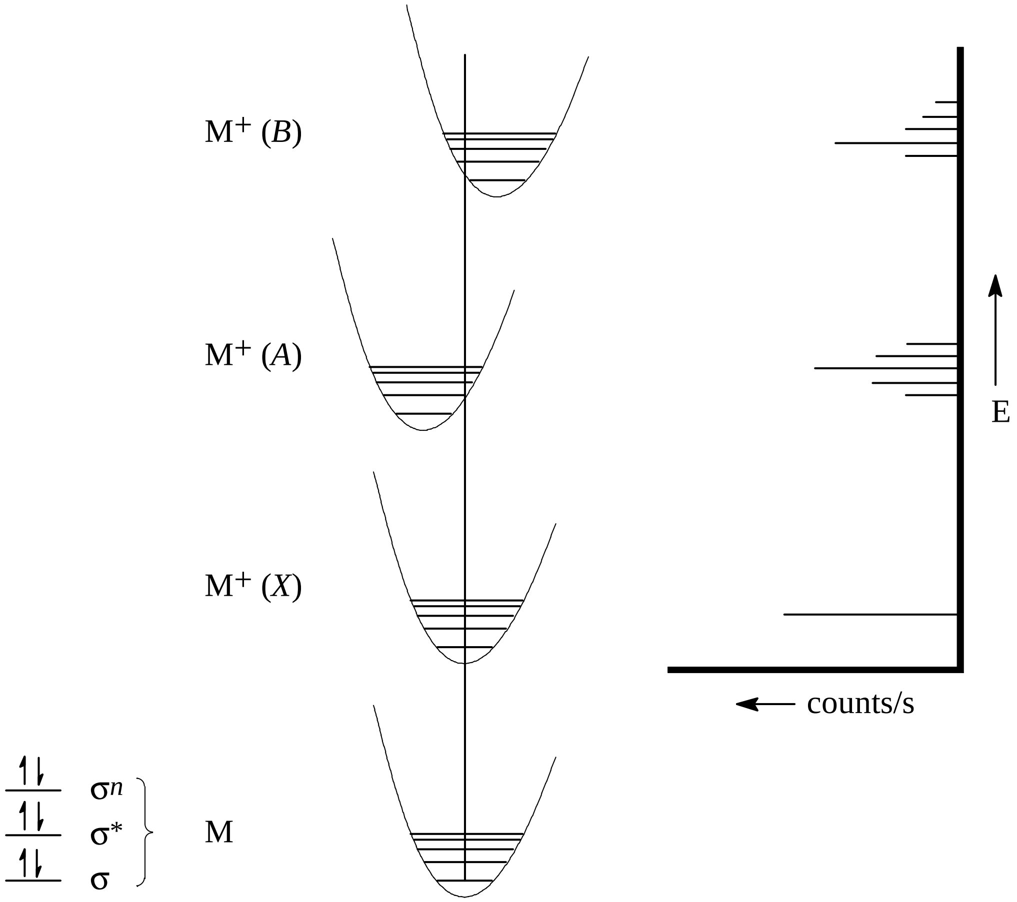
- At room temperature, most M molecules are in their vibrational ground state, v = 0.
- Ionization to M^+ can result in an ion in any of its possible electronic states, each of which may be in any of their allowed vibrational states, v'.

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.

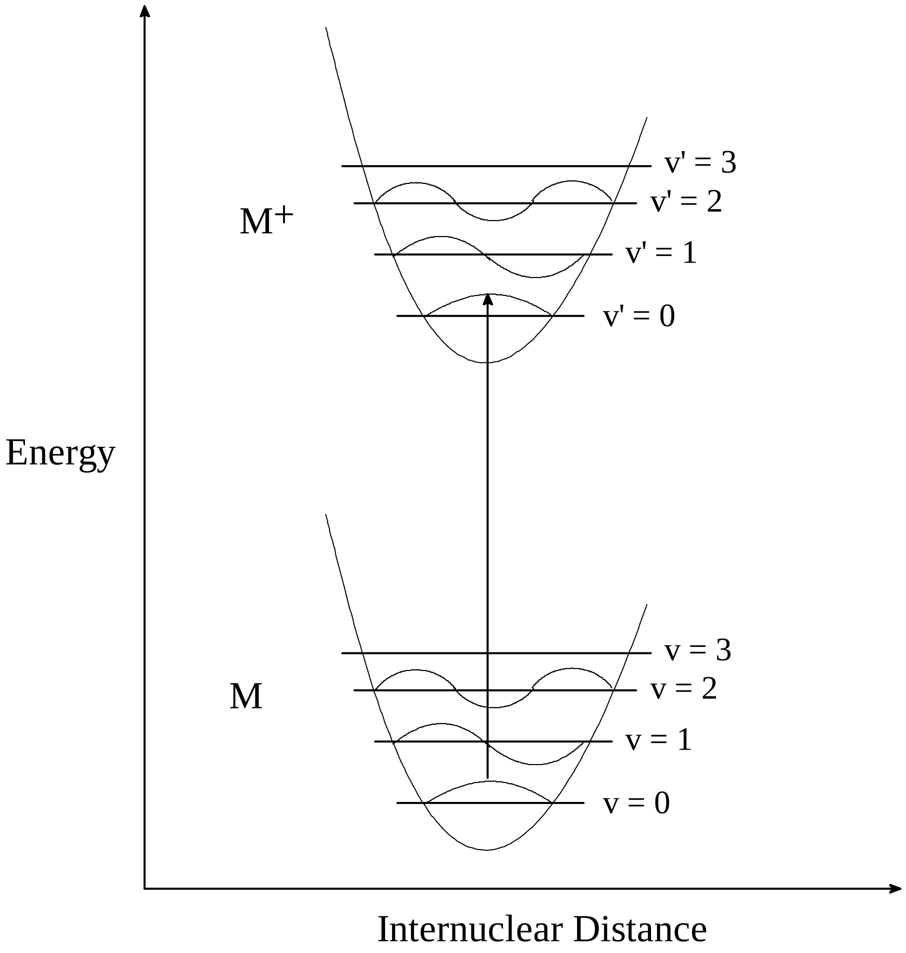
- The $v = 0$ state of M has maximum wave-function amplitude at the center of the bond, so a vertical transition always occurs from that position.

- If bond strength is unaffected by ionization, the strongest peak will correspond to $M\ (v = 0) \rightarrow M^+\ (v' = 0)$.

- If bond strength is changed by ionization, the strongest peak will correspond to $M\ (v = 0) \rightarrow M^+\ (v' > 0)$.

- Transitions to other v' states will have lesser intensities, varying according to their probabilities (*Franck-Condon distribution*).

Molecular Ionization from a Non-Bonding MO

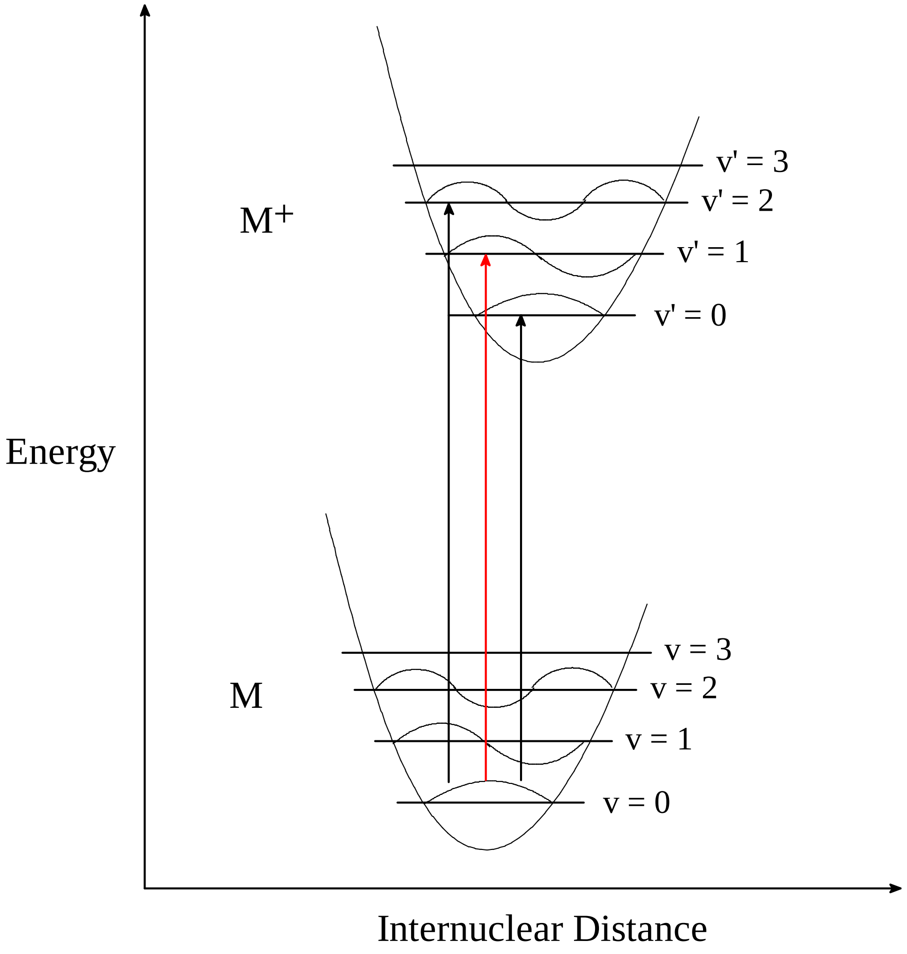


- Ionization from a non-bonding M.O. does not change bond length, so the vertical transition is the adiabatic transition, M (v = 0) → M^+ (v' = 0).

- Transitions to other v' states (other Franck-Condon transitions) have much less probability, due to the poor overlap between Ψ(v = 0) and Ψ'(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



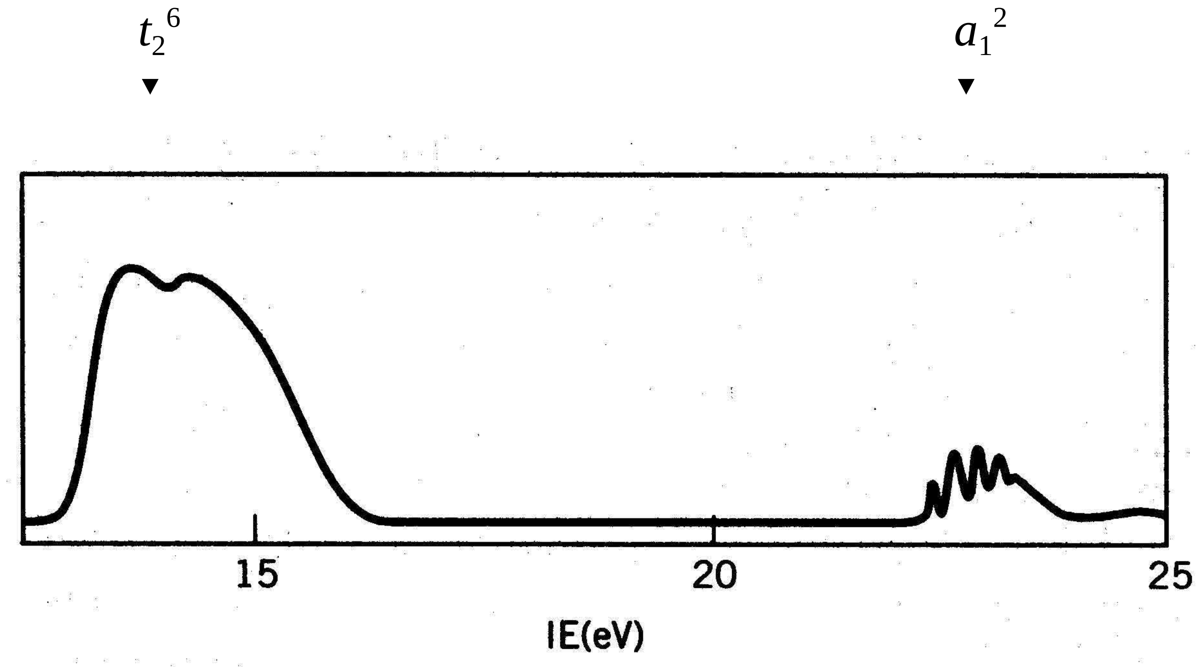
- Ionization from a bonding or anti-bonding M.O. causes a change in bond length in the ion M^+, compared to the bond length in M.
- The vertical transition is to an M^+ vibrational state v' > 0 with maximum wave-function overlap at the same inter-nuclear separation as the normal bond length of the neutral 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.

P.E.S. of CH_4 Revisited



✔ Both bands show vibrational fine structure, consistent with ionizations from bonding MOs.

✔ The band intensities and energies are consistent with the CH_4 MO scheme prediction of the electronic configuration: $(a_1)^2(t_2)^6$.