

Born-Oppenheimer Approximation

Adiabatic Assumption: Nuclei move so much more slowly than electron that the electrons that the electrons are assumed to be obtained if the nuclear kinetic energy is ignored, i.e., solve for the electronic wavefunctions with stationary nuclei.

The complete molecular Hamiltonian (neglecting magnetic terms) is:

$$\begin{aligned}
 H &= -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}} \\
 &- \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \sum_i \sum_{j > i} \frac{e^2}{r_{ij}} \\
 &= T_N + T_e + V_{NN} + V_{Ne} + V_{ee}
 \end{aligned}$$

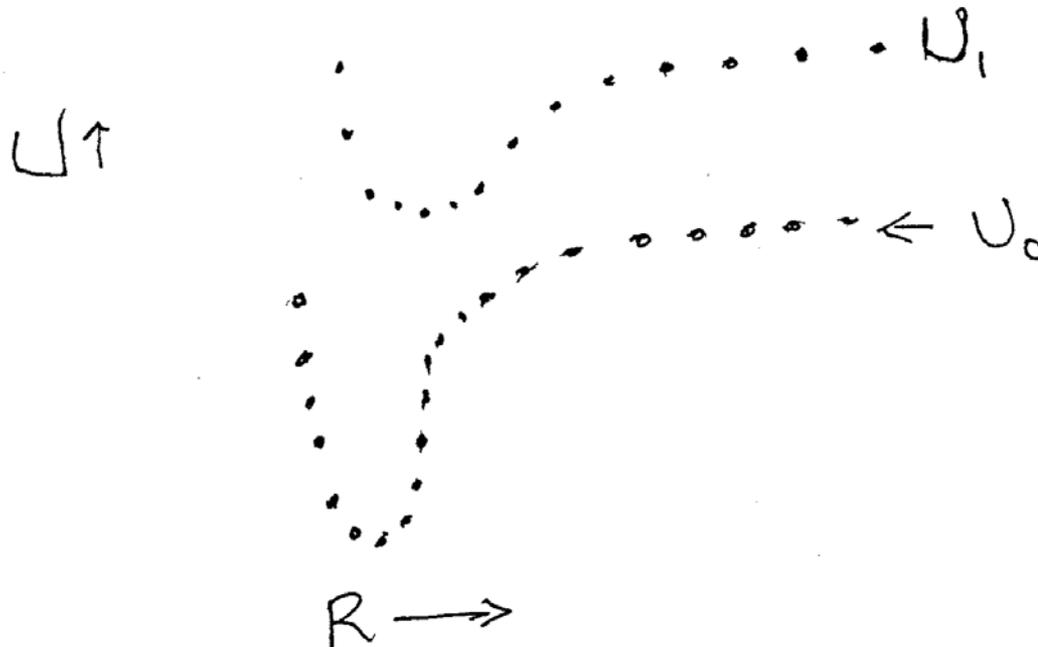
Define $H_{el} = T_e + V_{Ne} + V_{ee}$

The **separation of time scales** allows the solution of $H_{el} \Psi_{el,n}(q_i; Q_\alpha) = E_{el,n}(Q_\alpha) \Psi_{el,n}(q_i; Q_\alpha)$ at a set of fixed nuclear configurations, Q_α for the ground and excited states, n . Adding on the V_{NN} also a function of Q_α gives:

$U_n(Q_\alpha) = E_{el}(Q_\alpha) + V_{NN}(Q_\alpha)$, which serves the potential energy for the nuclei.

$U_n(Q_\alpha)$ are called Born-Oppenheimer potential (energy) surfaces.

The $U_n(Q_\alpha)$ look like:

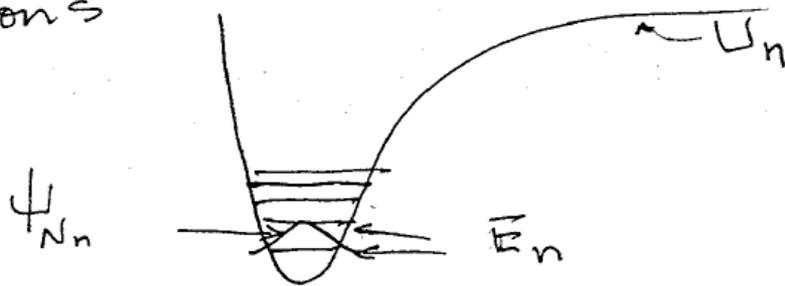


The $U_n(q, \alpha)$ are effective potential energy functions for the nuclear motion, to be used in the nuclear Schrodinger equation:

$$H_N = T_N + U_n(q, \alpha)$$

$$H_N \psi_N(q, \alpha) = E_n \psi_N(q, \alpha)$$

The ψ_N are similar to harmonic oscillator wave functions



One now defines the

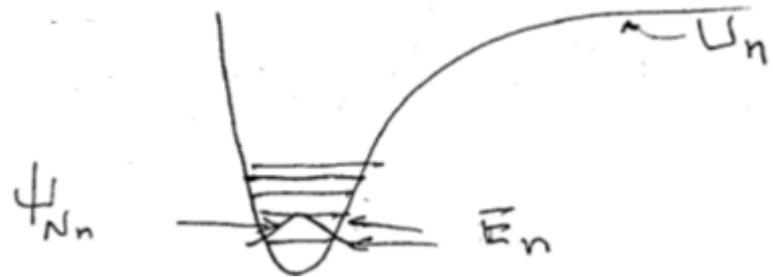
nuclear Hamiltonian as $H_{Nn} = T_N + U_n(Q_\alpha)$

and solves the nuclear Schrodinger Equations on these surfaces:

$$H_{Nn}\phi(Q_\alpha) = E_n\phi(Q_\alpha)$$

The low energy solutions $\phi(Q_\alpha)$ will look very much like harmonic oscillator eigenfunctions:

$$\Psi_{BO} = \Psi_{el,n}(q_i; Q_\alpha) \phi(Q_\alpha)$$



The semicolon in $\Psi_{el,n}(q_i; Q_\alpha)$ means the electronic function depends only **parametrically** on Q_α (i.e., does not appear explicitly in $\Psi_{el,n}(q_i; Q_\alpha)$). It nevertheless depends very much on Q_α because the electron density follows the nuclei.

The separability implied by the Born-Oppenheimer (BO) wavefunction says that the electrons instantly adjust their state to the nuclear zero point motions.

The BO wavefunction is exactly true only if:

$$\nabla_{\alpha}^2 \Psi_{el,n}(q; Q_{\alpha}) \Phi(Q_{\alpha}) = \Psi_{el,n}(q; Q_{\alpha}) \nabla_{\alpha}^2 \Phi(Q_{\alpha})$$

This is not quite true because $\nabla_{\alpha}^2 \Psi_{el,n}(q; Q_{\alpha}) \neq 0$

due to the atomic orbitals effectively floating along with the nuclear positions, the effect is small most of the time.

The effect of the 2nd derivative with respect to nuclear positions is called "**Born-Oppenheimer breakdown**", and is responsible from excited state phenomena such as the conversion of electron energy into nuclear kinetic energy (heat).

The Born-Oppenheimer wavefunction:

$$\Psi_{BO} = \Psi_{el,n}(q; Q_\alpha) \Phi_N(Q_\alpha)$$

says that the electrons instantly adjust their state to the nuclear positions. It is interesting to view the Born-Oppenheimer wavefunction as a kind of linear combination of the $\Psi_{el}(q_i; Q_\alpha)$. A wavefunction can be thought of as a big vector of numbers, one for each point in space.

The B-O wavefunction has the amplitude for the electrons being at being at points in space when the nuclei are at Q_α multiplied by $\Phi_N(Q_\alpha)$, the amplitude for the nuclei to be at the points Q_α .

The probability density is therefore:

(probability density for a certain nuclear configuration) x (probability density for the electrons when the nuclei are at that nuclear configuration)

Matrix Elements Between B-O Vibronic States.

We will want to know how to find matrix elements of the Hamiltonian that couple different molecular states because we shall see when we study time-dependent quantum mechanics that:

the **rate of transition** between states m and n is proportional to $|\mathbf{H}_{mn}|^2$

State functions of the B-O type are often called *vibronic* states, because they describe both electronic and vibrational coordinates.

Consider a matrix element of the Hamiltonian (but it could be any other operator) coupling two B-O states m and n ,

$$H_{mn} = \langle \Psi_{el,m}(\mathbf{q}_i) \Phi_{N,m}(Q_\alpha) | H | \Psi_{el,n}(\mathbf{q}_i) \Phi_{N,n}(Q_\alpha) \rangle$$

Since $H = H(\mathbf{q}_i, Q_\alpha)$, and Ψ_N depends only on Q_α , we integrate first only over \mathbf{q}_i

$$= \langle \Phi_{N,m}(Q_\alpha) | \langle \Psi_{el,m}(\mathbf{q}_i) | H | \Psi_{el,n}(\mathbf{q}_i) \rangle_{\mathbf{q}_i} | \Phi_{N,n}(Q_\alpha) \rangle_{Q_\alpha},$$

where the subscripts indicate the integration variable. This gives

$$H_{mn}(Q_\alpha) = \langle \Phi_{N,m}(Q_\alpha) | \langle \Psi_{el,m}(\mathbf{q}_i; Q_\alpha) | H | \Psi_{el,n}(\mathbf{q}_i; Q_\alpha) \rangle_{\mathbf{q}_i} | \Phi_{N,n}(Q_\alpha) \rangle_{Q_\alpha}$$

Often $H_{mn}(Q_\alpha)$ is not very sensitive to Q_α , i.e., is essentially constant with the value at the equilibrium geometry, Q_e . (This is known as the **Condon Approximation**). Then it comes out of the integral to give:

$$H_{mn} = H_{mn}(Q_e) \langle \Psi_{N,m}(Q_\alpha) | \Psi_{N,n}(Q_\alpha) \rangle_{Q_\alpha}, \text{ so that}$$

$$|H_{mn}|^2 = |H_{mn}(Q_e)|^2 \langle \Phi_{N,m}(Q_\alpha) | \Phi_{N,n}(Q_\alpha) \rangle_{Q_\alpha}^2 = |H_{mn}(Q_e)|^2 \mathbf{F}_{mn}$$

The overlap integral squared of the nuclear wave functions for the two states (in bold) is called the **Franck-Condon** factor, \mathbf{F}_{mn} . $\mathbf{F}_{mn} = 1$ only if the equilibrium nuclear positions and the force constants for stretching and bending bonds are the same in states m and n . This is seldom the case because when electrons change state, e.g., during absorption of light or electron transfer, the electron densities in the bonds change, making the bond lengths and/or angles change.

The Independent Harmonic Oscillator Model for $\Phi_N(Q_\alpha)$: Normal Modes

Just as we take products of orbitals (independent electrons) as a starting point for the electronic wavefunction, when there are more than two nuclei we are faced with typically $3N-6$ vibrational coordinates, where N = the number of nuclei ($3N-5$ for linear molecules), which only have two rotational degrees of freedom). In the limit of *harmonic* springs connecting neighboring atoms, one can diagonalize the mass weighted force-constant matrix and obtain eigenvectors (normal modes of vibration) describing concerted, correlated motion of the atoms). It is as if there are $3N-6$ independent oscillators, so the wavefunction can be written as

$$\begin{aligned}\Phi_N(Q_\alpha) &= \prod_{\alpha=1}^{3N-6} \phi_{v_\alpha}(Q_\alpha) \\ &= \phi_{v_1}(Q_1)\phi_{v_2}(Q_2)\phi_{v_3}(Q_3)\dots\phi_{v_{3N-6}}(Q_{3N-6})\end{aligned}$$

where $\phi_{v_\alpha}(Q_\alpha)$ is a harmonic oscillator energy eigenfunction for the vibrational coordinate Q_α , and v_α is a harmonic oscillator quantum number for the particular vibrational normal mode.

The Franck-Condon factor then separates into a product: $F_{mn} = \prod f_{nm,\alpha}$

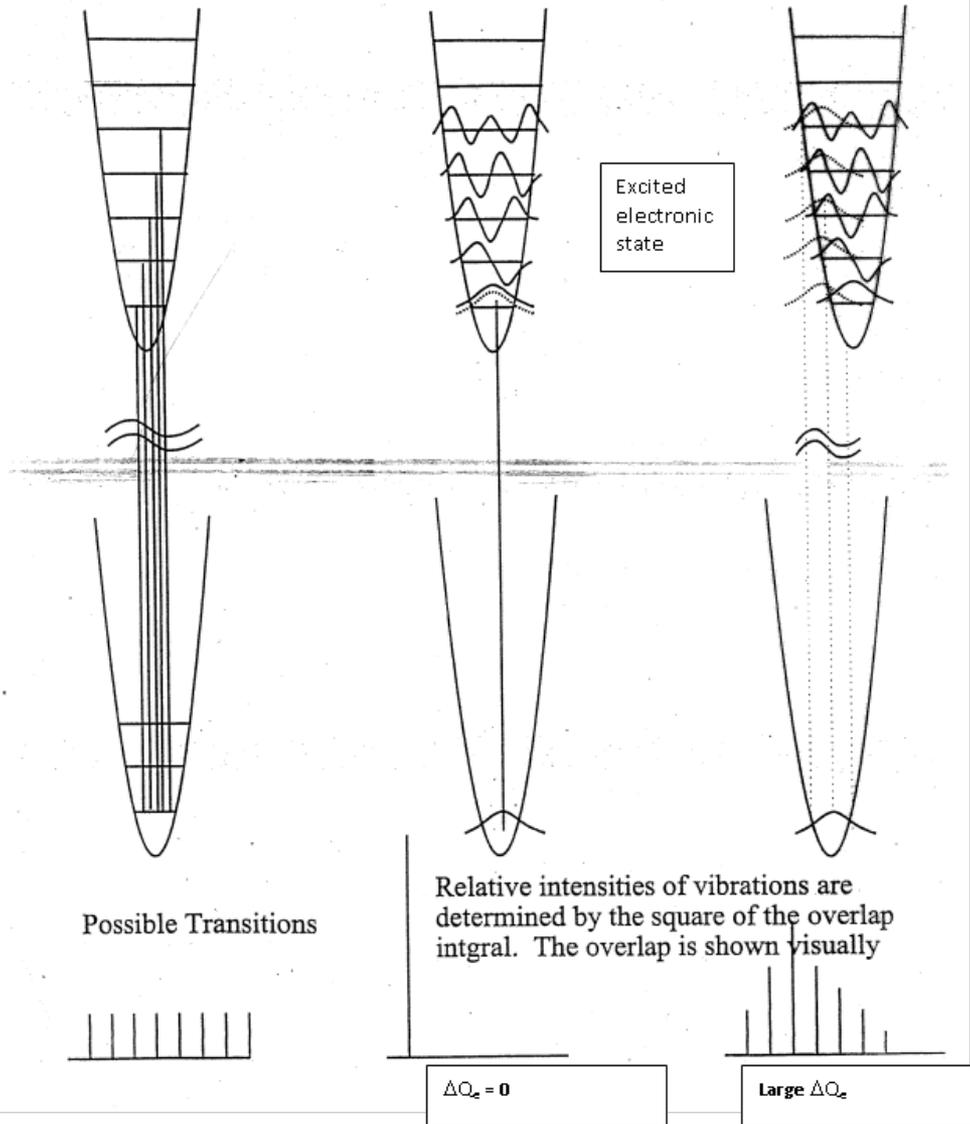
where $f_{nm,\alpha} = |\langle \phi_{vm\alpha}(Q_\alpha) | \phi_{v'n\alpha}(Q_\alpha) \rangle|^2$

The Franck-Condon factors are most sensitive to the difference in the equilibrium nuclear positions between the initial and final states, ΔQ_e as is demonstrated in the figure below.

When the vibrational frequency difference is not very different between the final and initial states, the FC factors are dominated by ΔQ_e . For the case of no frequency change it is seen that the ground vibrational wavefunction has an overlap = 1.0 for the 0-0 transition, and exactly 0 for all other vibronic transitions due to the orthogonality the harmonic oscillator functions.

Frank - Condon Factors

Drawn by Prof.
Lee Spangler



For the case of harmonic and zero frequency change, the FC factors are given by the associated Laguerre polynomials:

$$\langle \phi_{v'}(Q) | \phi_{v''}(Q) \rangle \equiv \langle v' | v'' \rangle = \left(\frac{s}{2^{1/2}} \right)^{v'-v''} \frac{v'! L_{v''-v'}^{v''-v'}(s^2/2)}{v''! v''!} e^{-s^2/4}, v'' > v'$$

where $s = \frac{\Delta Q_e}{Q_{oc}}$ and $Q_{oc} = \left(\frac{\hbar}{\mu\omega} \right)^{1/2}$ and $\mu =$ the reduced mass, $\omega =$ circular frequency

You will recall from homework #1 that Q_{oc} is the classical turning point in the $v=0$ state of the harmonic oscillator, and use as physically meaningful unit of length, serving the same purpose as the Bohr radius does in atomic units.

s is therefore the change in equilibrium amplitude of the oscillator in units of the

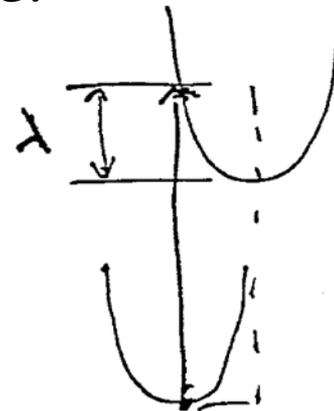
extension of the oscillator to the point where $\frac{1}{2}k \Delta Q_{oc}^2 = \frac{1}{2} h \nu$

Most commonly, the initial state is $v' = 0$, which reduces the general equation to the simple form that is (interestingly) the **Poisson Distribution**:

$$f_{0v''} = |\langle 0 | v'' \rangle|^2 = \frac{\lambda^{v''}}{v''!} e^{-\lambda}$$

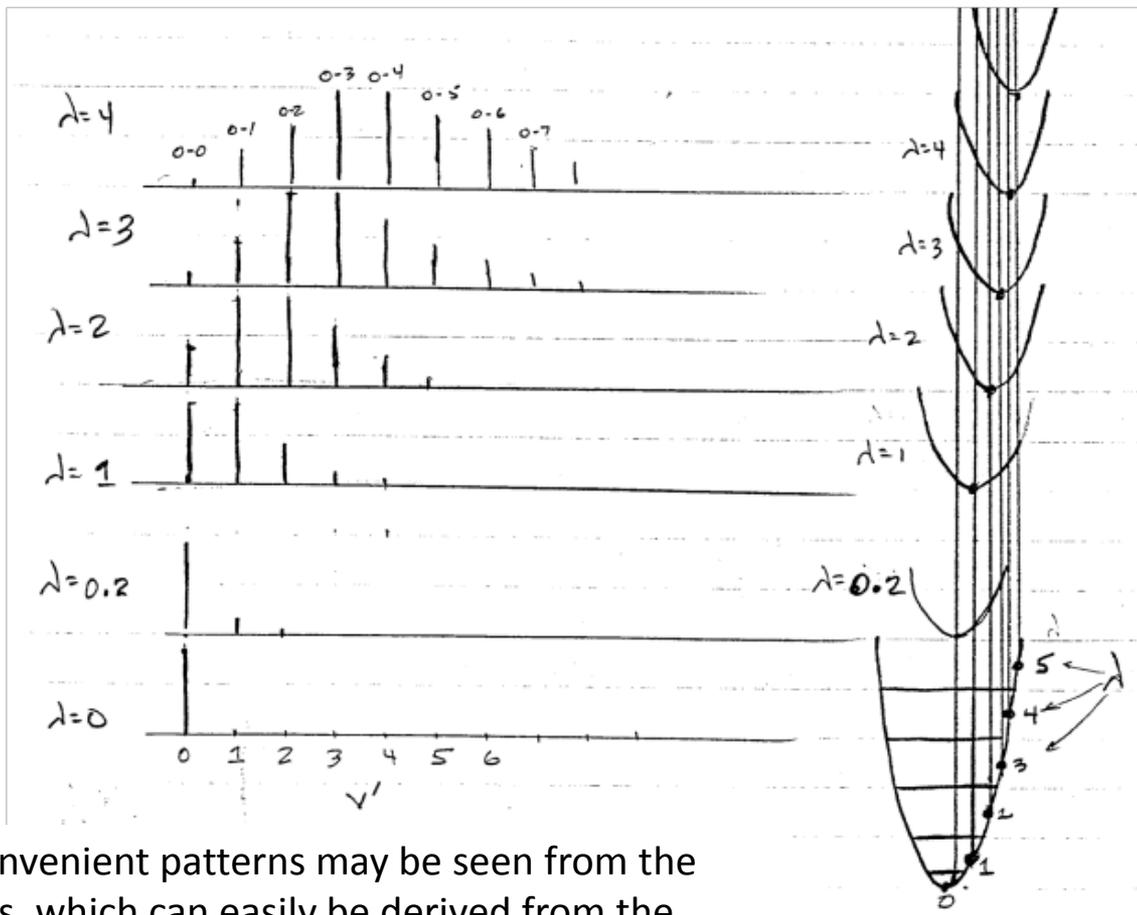
The meaning of λ simple and tangible because:

$$\lambda = \frac{1}{2} s^2 = \frac{1}{2} \frac{Q_e^2}{Q_e^2} = \frac{1}{2} \frac{\mu \omega Q_e^2}{\hbar} = \frac{1}{2} \frac{\mu \omega^2 Q_e^2}{\hbar \omega} = \frac{1}{2} \frac{k Q_e^2}{\hbar \omega}$$



It is the instantaneous spring potential energy in units of $h\nu$ caused by the instantaneous shift of the potential energy function (shift of Q_e)—*while the nuclear wave function remains unchanged*.

Below is a fairly quantitative depiction of what the FC progressions look like for a few selected values of λ .



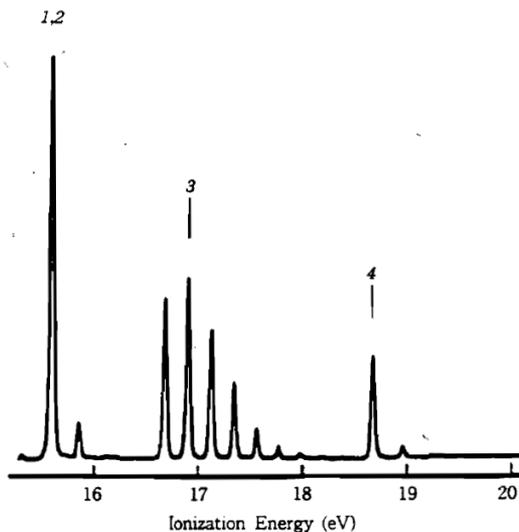
Two convenient patterns may be seen from the pictures, which can easily be derived from the Poisson equation:

$$\frac{f_{0,v''}}{f_{0,v''-1}} = |\langle 0 | v'' \rangle|^2 = \frac{\lambda^{v''} (v''-1)!}{v''! \lambda^{v''-1}} = \frac{\lambda}{v''}$$

which give $\frac{f_{0,1}}{f_{0,0}} = \lambda$

and $f_{0,v''-1} = f_{0,v''}$ when $v'' = \lambda$

Below are figures of the photoelectron spectra of N₂ and CO gas. They are similar to electron absorption spectra except that they come from shining x-rays that are high enough in energy to ionize most of the higher lying electrons. The spectrum are actually measurements of kinetic energy of the released electrons, from which the ionization energy can easily be calculated.

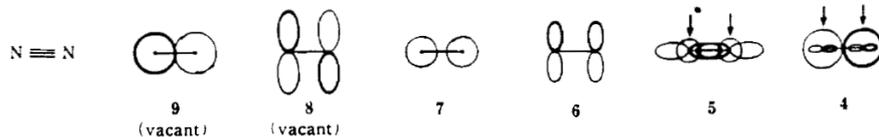
(7) N₂ Nitrogen

	Exptl. ^{a)} <i>I_v</i> (eV)	SCF MO [6-31 G] ^{b)}		CI (Ionic State) [6-31 G] ^{c)}			
		- <i>ε</i> (eV)	MO	Character	<i>E</i> (eV)	State	Configuration
1	15.60	16.93	1π _u (6, 7)	π _{bond}	14.93	1 ² Σ _g ⁺	0.93(5 ⁻¹)
2	15.60	16.93					+0.12(4 ⁻¹ , 6 ⁻¹ , 8 ¹) _g
							-0.12(4 ⁻¹ , 7 ⁻¹ , 9 ¹) _g
							-0.11(5 ⁻¹ , 6 ⁻² , 8 ²)
							-0.11(5 ⁻¹ , 7 ⁻² , 9 ²)
3	16.98	17.13	3σ _g (5)	σ _{NN}	16.62	1 ² Π _u	0.95(6 ⁻¹)
							-0.13(6 ⁻¹ , 7 ⁻² , 9 ¹)
							-0.12(6 ⁻² , 7 ⁻¹ , 8 ¹ , 9 ¹) _g
4	18.78	21.08	2σ _u (4)	N _{2s}	18.38	1 ² Σ _u ⁺	0.91(4 ⁻¹)
							+0.20(5 ⁻¹ , 6 ⁻¹ , 8 ¹) _g
							-0.20(5 ⁻¹ , 7 ⁻¹ , 9 ¹) _g
							-0.11(4 ⁻¹ , 6 ⁻² , 8 ²)
							-0.11(4 ⁻¹ , 7 ⁻² , 9 ²)

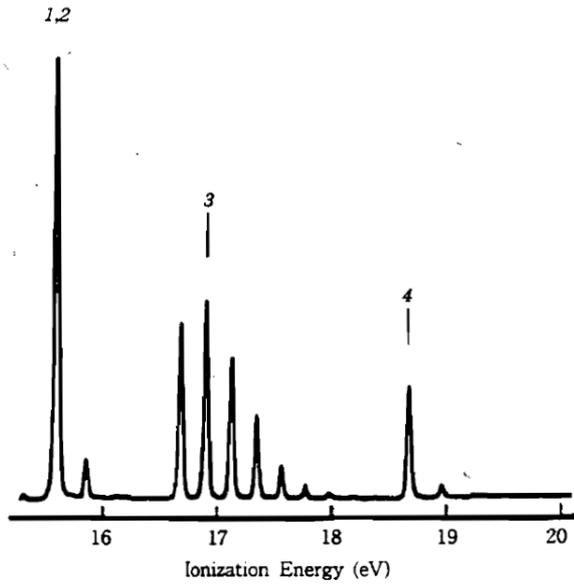
a) The spectrum: this work. The *I_v*'s: Turner *et al.* (215). See also other works: Turner and May (215 a); Edqvist *et al.* (90); Carlson and Jonas (54); Okuda and Jonathan (171); Natalis *et al.* (165); Gardner and Samson (104, 105); Lee and Rabalais (149); and Potts and Williams (182 a).

b) We used the bond length reported (A 2); symmetry *D_{∞h}*. *E*_{SCF} = -108.8678 hartree. In 4-31 G calculations, *E*_{SCF} = -108.7537 hartree and -*ε*(eV) = 16.90, 16.90, 17.11, and 21.03.

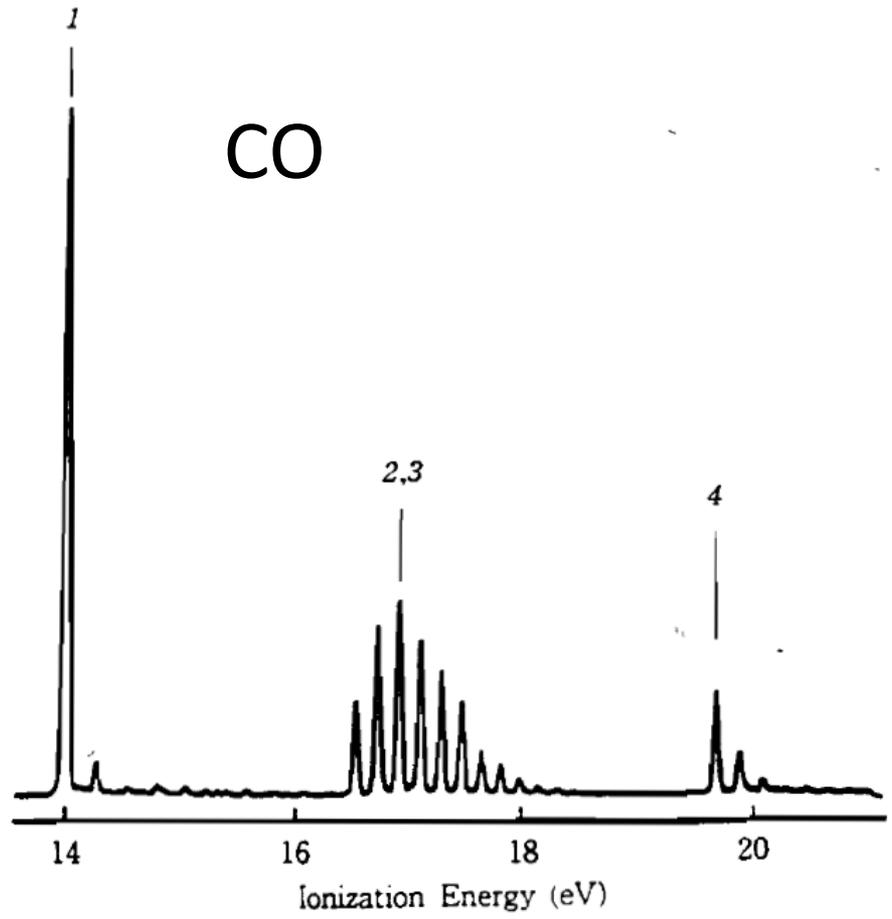
c) CI-II. (8, 9) = 1π_g. |*N*⟩ = 0.96 (SCF) - 0.11 (6⁻², 8⁻²) - 0.11 (7⁻², 9²) - 0.10 (6⁻¹, 7⁻¹, 8¹, 9¹)_g. The results obtained in other CI levels are given in Appendix B.



N_2



CO



Using the equations above for λ , the Franck-Condon pattern reveals from what type of MO of electron has been ejected. If it was a strongly bonding MO there will be large change in Q_e and therefore λ will be large and a long progression will be seen, as for the 2nd ionization potential for both molecules.

In both cases, the 1st ionization exhibits a quite small λ , strongly implying that the electron came from a non-bonding MO.

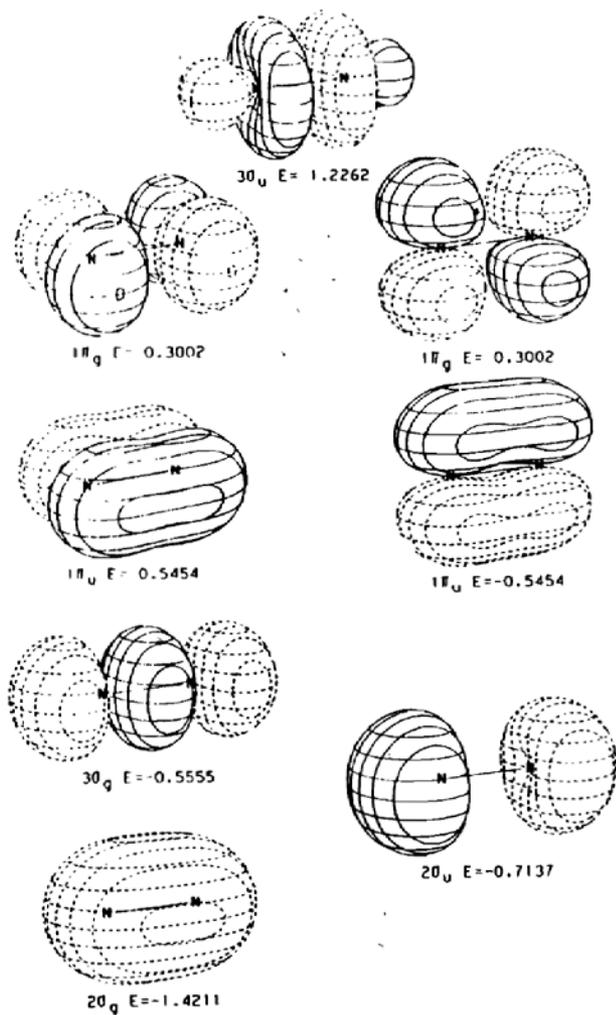
The next slide shows some predictions using Koopman's theorem, published in a book by Jorgenson and Salem.

The calculations imply that 1st ionization for N_2 should come from the 2p pi bonding MO, but the experiment clearly does not support that.

Agreement for CO_2 is, however, qualitatively correct.

16. Nitrogen

Symmetry: $D_{\infty h}$



15. Carbon Monoxide

Symmetry: $C_{\infty v}$

