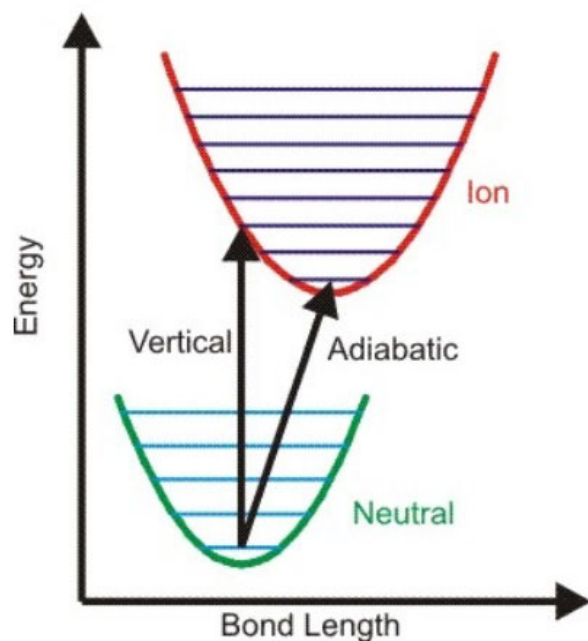


Electronic spectroscopy including photoelectron spectroscopy



If the molecule is cold, and doesn't have very low frequency vibrations, only $v=0$ is populated in the ground electronic state.

The vibrational structure accompanying electronic excitation is given by the overlap of $v=0$ of the ground state with the various $v=1$ levels of the excited state. (Franck-Condon approximations).

If the excited potential is unshifted and same shape as the ground state potential, the spectrum would have a single line (the $0 \rightarrow 0$ transition).

If the excited state curve is appreciably shifted (large change in geometry), the transition will be accompanied by a long progression.

The peak in the progression corresponds to the vertical transition

If the distortion upon excitation is large, one might not even see the $(0,0)$ transition.

The figures on this slide and the next three slides are from chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/10%3A_Bonding_in_Polyatomic_Molecules/10.04%3A_Photoelectron_Spectroscopy

FC approximation for transition between electronic state 0 to electronic state i

$$\langle \psi_0^{el} \psi_{0,0}^{vib} | \mu | \psi_i^{el} \psi_{i,j}^{vib} \rangle \approx \langle \psi_0^{el} | \mu(R_e) | \psi_{i,j}^{vib} \rangle \langle \psi_{0,0}^{vib} | \psi_{i,j}^{vib} \rangle$$

The intensity is proportional to the absolute value squared of this quantity.

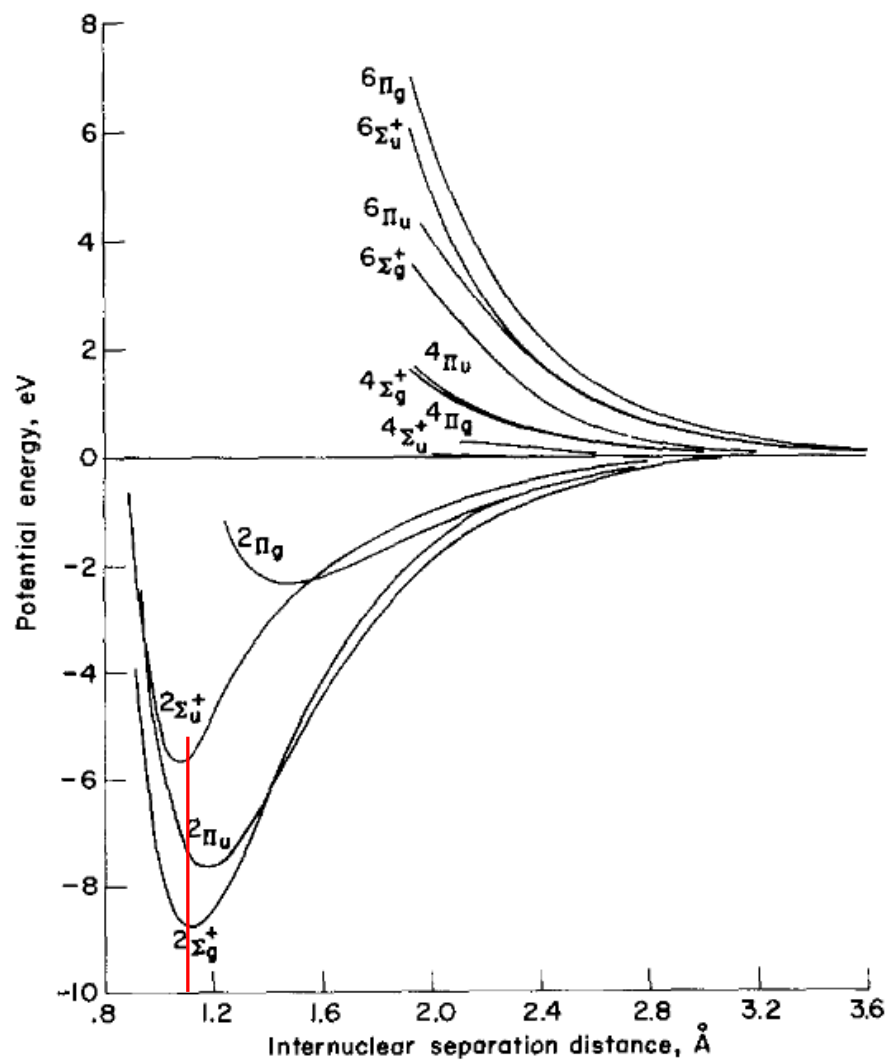
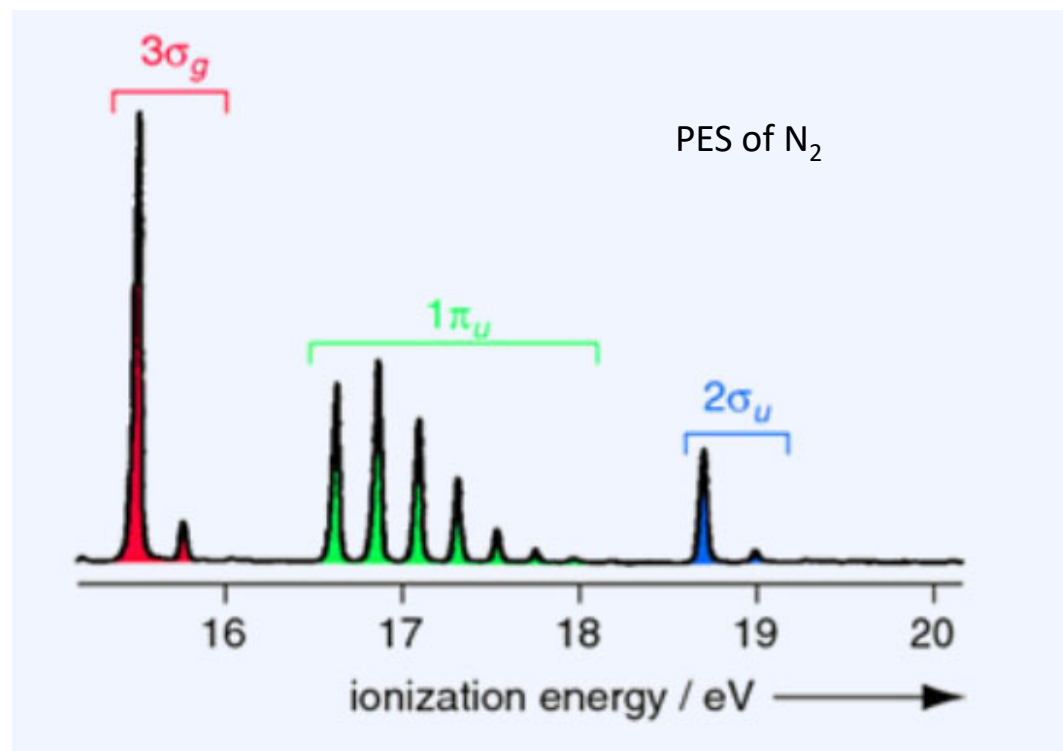
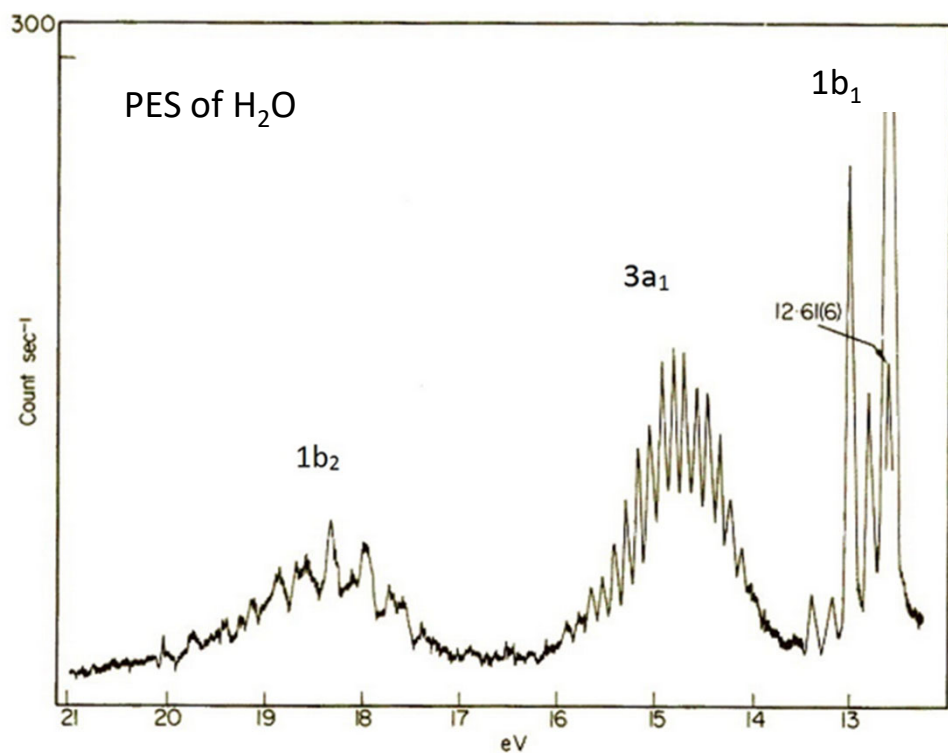


FIG. 1. Potential-energy curves for $N_2^+ \rightarrow N(^4S^0) + N^+(^3P)$.



The vertical red line, indicates the equilibrium bond length of neutral N_2



Note how long the progression is when ionizing from the valence a₁ orbital and that this is a progression in the low-frequency bending vibration.

When ionizing from the 1b₁ two different vibrations are excited

Kasha's rule (for molecules in the condensed phase)

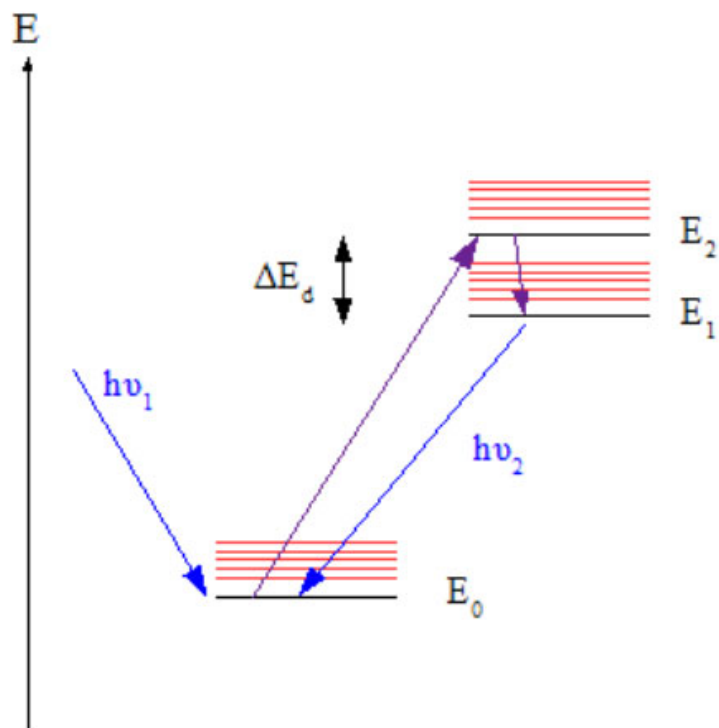


Figure from Wikipedia

in the condensed phase a molecule which is formed vibrationally excited in an electronically excited state, can be vibrationally relaxed due to "collisions", causing the absorption and emission spectra to differ.

Moreover, if the system is prepared into an upper electronic state (say S_2), collisions cause rapid decay to the lowest excited state (S_1). (Recall S denotes a singlet; if spin is a good quantum number, collisions probably won't cause conversion to the still lower-lying triplet states)

Ex. Diphenyloctatetraene: abs. max. at 3.3 eV, emission max at 2.4 eV

There is a dipole-forbidden doubly-excited state energetically below the dipole-allowed singlet state. Do you see how that can happen?