



ENGINEERING CHEMISTRY

Department of Science and Humanities

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Module I- Molecular Spectroscopy



Class content:

- ***Intensity of spectral lines***
- ***Franck Condon Principle***

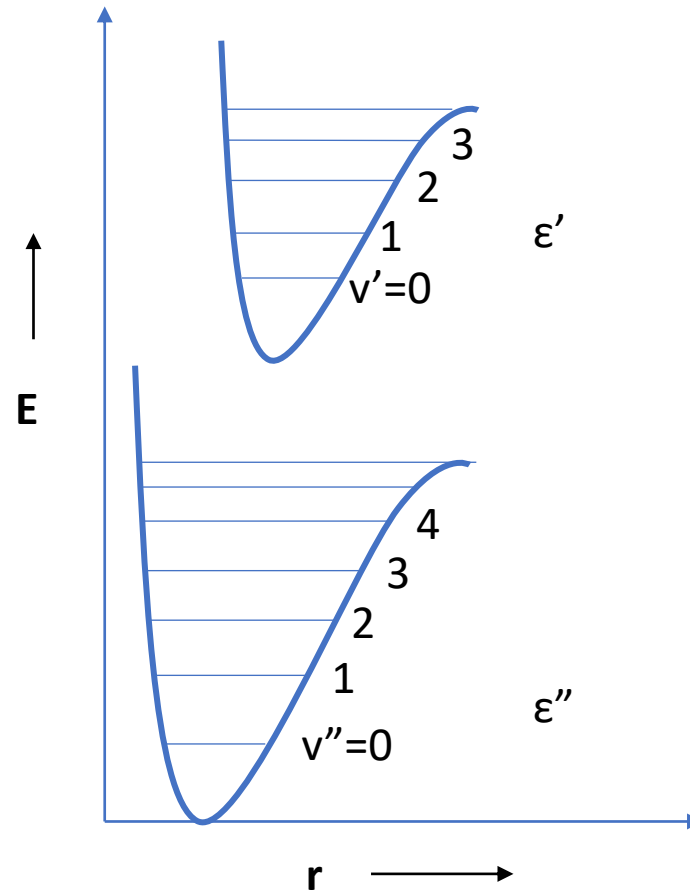
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Electronic spectroscopy

Intensity of spectral lines

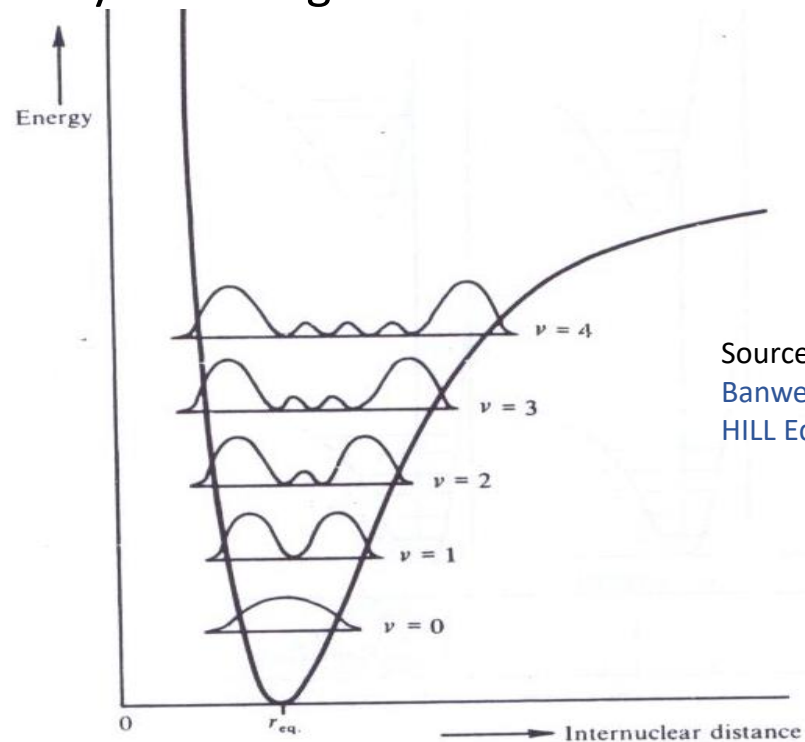
- There are **no selection rules** for vibrational changes during an electronic transition
- Most of the **transitions start from $v''=0$** as it is most populated level
- The excited state usually has **longer internuclear distance** because of antibonding character



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The transitions arise from the **centre of $v''=0$** because the maximum probability of finding the nuclei is at the centre of $v''=0$



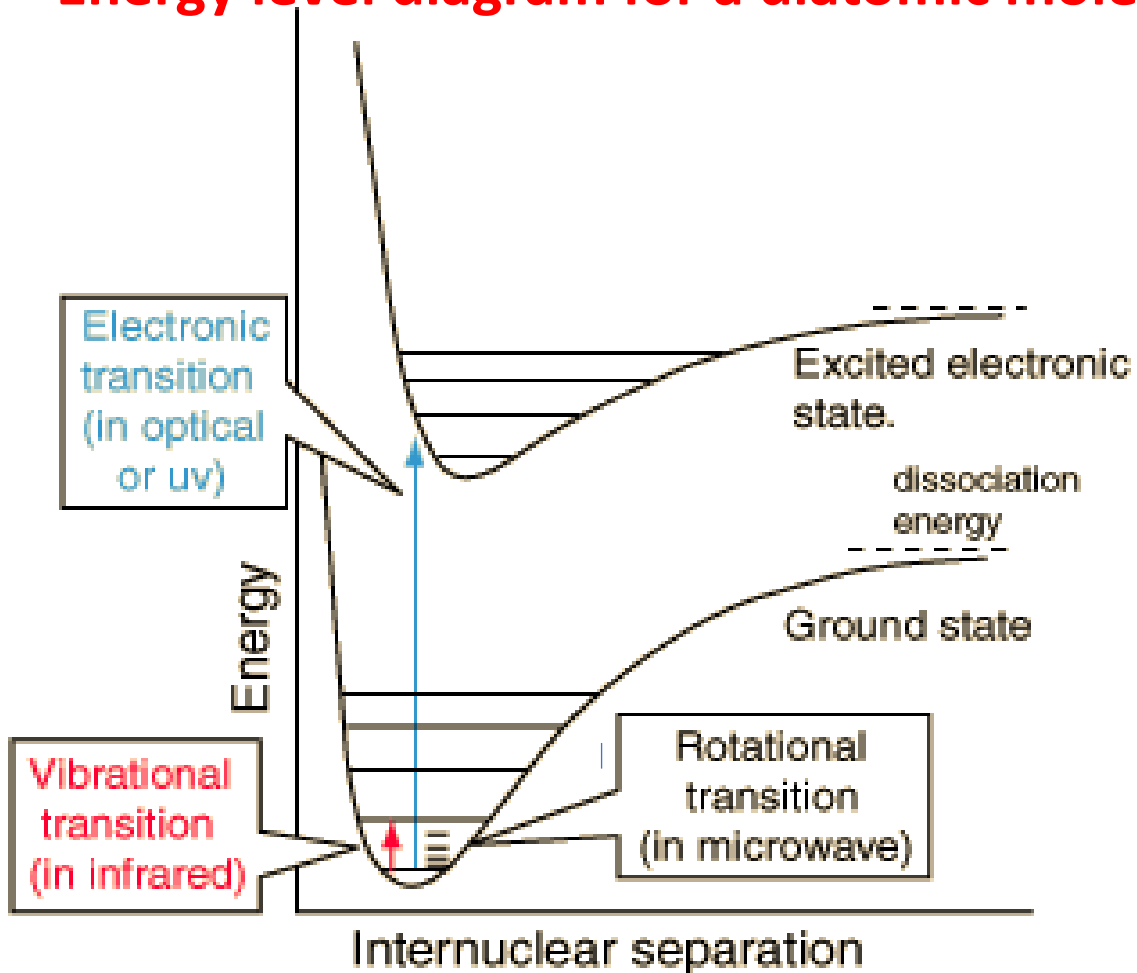
Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

Probability distribution for a diatomic molecule according to quantum theory

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Energy level diagram for a diatomic molecule



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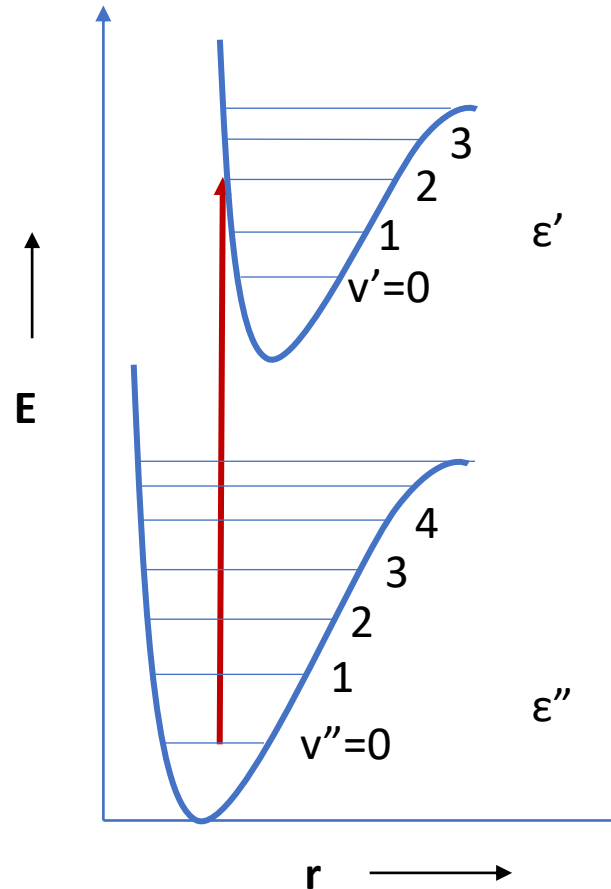
Franck-Condon principle

- All lines in the spectra are **not of the same intensity** though no selection rule for vibrational transitions exist

Statement of Franck Condon principle:

“An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition”

- This implies that the electronic transitions are always **vertical transitions**



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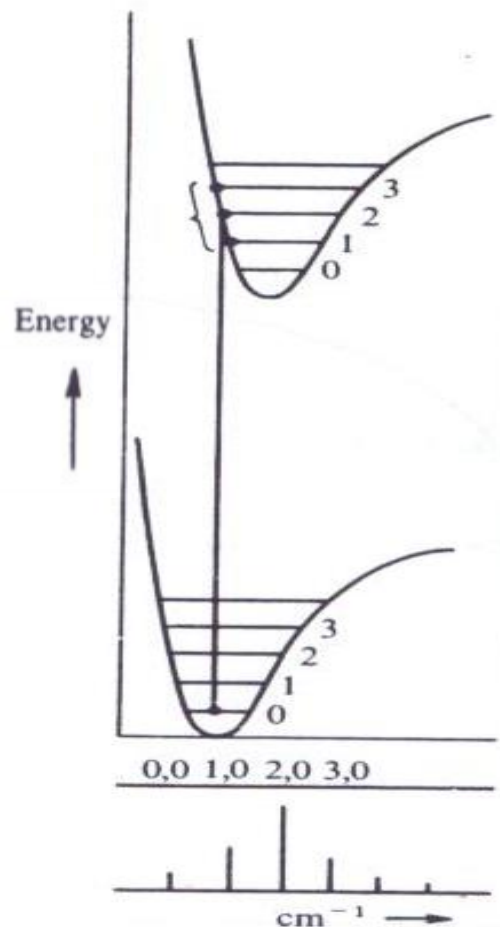
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r_e'' and r_e' are the internuclear distances of the ground and excited states respectively

Three possibilities of vibrational - electronic transitions exist

- **Internuclear distance of excited state is more than that of ground state $r_e'' < r_e'$**

The spectrum shows **maximum intensity for ($v',0$) line** where v' is the vibrational level in the excited state to which electronic transition takes place



Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

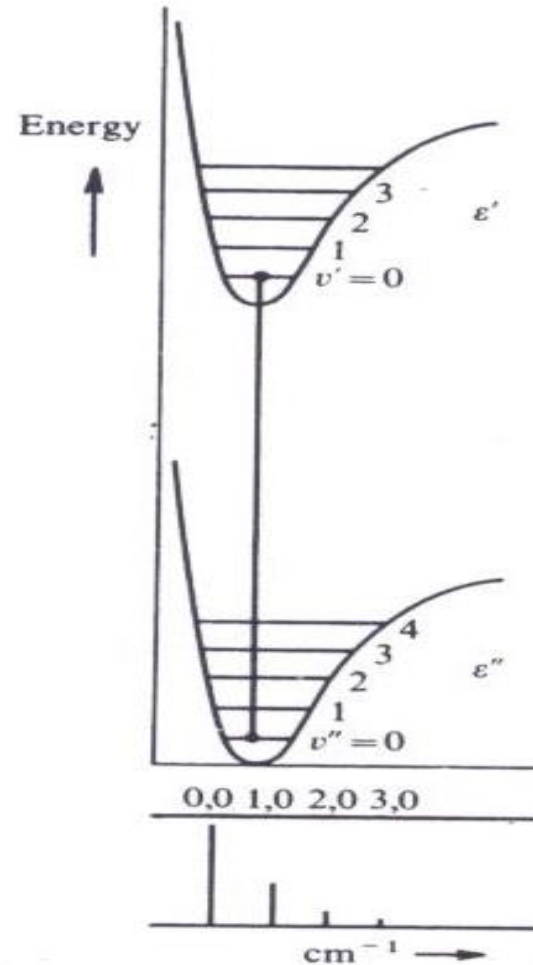
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- No change in internuclear distance

$$r_e'' = r_e'$$

The spectrum shows **maximum intensity for (0,0) line** and intensity falls for the remaining lines



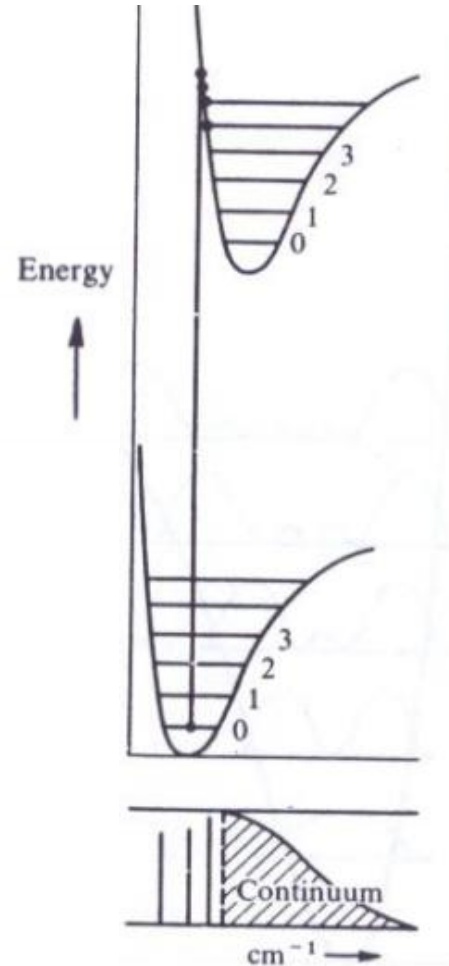
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- Internuclear distance of excited state is considerably greater than that of ground state $r_e'' \ll r_e'$

The spectrum shows **continuum** since the transition results in the molecule going beyond dissociation energy. The molecule dissociates into atoms which gain kinetic energy. Since this energy is not quantised a continuum is seen in the spectrum



Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.



THANK YOU

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