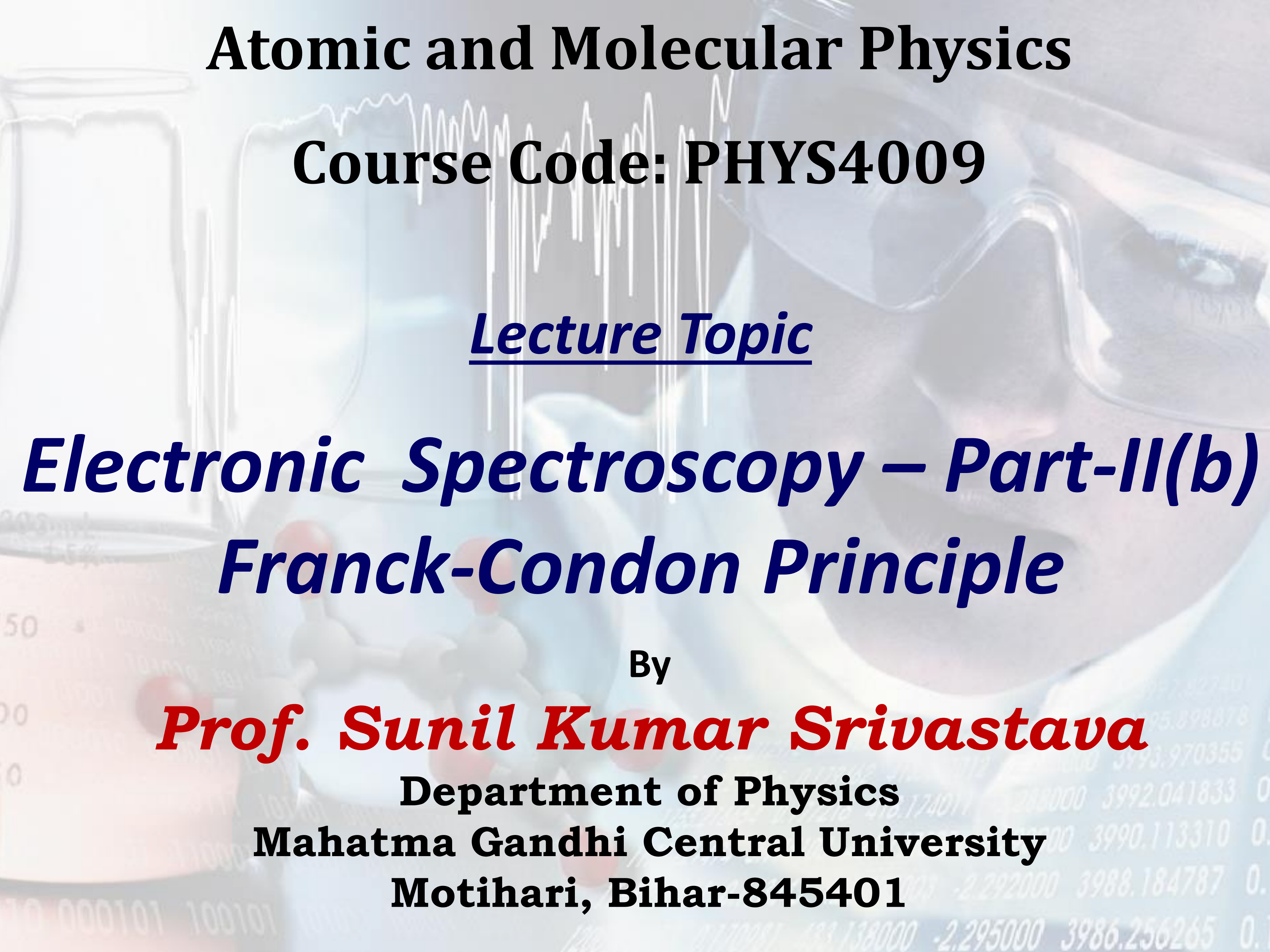

Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Electronic Spectroscopy – Part-II(b)
Franck-Condon Principle

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Outline

- *What are Molecular Orbitals?*
- *Types of Molecular Orbitals*
- *Electronic Configuration of the Molecule*
- *Molecular Electronic States*

Part - I

- *Electronic Transitions*
- *Rotational Fine Structure*
- *Fortrat Diagram*

Part – II(a)

- *Franck Condon Principle*
- *Application of Electronic Absorption Spectroscopy*

Part – II(b)
Current

Born-Oppenheimer Approximation

In a molecule the kinetic energy T consists of contributions from the motions of the electrons and nuclei i.e. T_e and T_n, respectively. The potential energy comprises two terms, V_{ee} and V_{nn}, due to coulombic repulsions between the electrons and between the nuclei, respectively, and a third term V_{en}, due to attractive forces between the electrons and nuclei, giving

$$H = T_e + T_n + V_{ee} + V_{nn} + V_{en}$$

For fixed nuclei $T_n = 0$, and V_{nn} is constant, and there is a set of electronic wave functions ψ_e which satisfy the Schrödinger equation

$$H_e \psi_e = E_e \psi_e$$

where, $H_e = T_e + V_{ee} + V_{en}$

Since H_e depends on nuclear coordinates, because of the V_{en} term, so do ψ_e and E_e but, in order to solve the Schrödinger equation, Born–Oppenheimer proposed an approximation in 1927, where it is assumed that vibrating nuclei move so slowly compared with electrons that ψ_e and E_e involve the nuclear coordinates as parameters only. The result for a diatomic molecule is that a curve of potential energy against internuclear distance r (or the displacement from equilibrium) can be drawn for a particular electronic state in which T_e and V_{ee} are constant. This is known as "**Born–Oppenheimer Approximation**"

According to Born–Oppenheimer approximation that the total wave function ψ can be factorized as:

$$\psi = \psi_e(q, Q)\psi_n(Q)$$

where the q are electron coordinates and ψ_e is a function of nuclear coordinates Q as well as q.

Franck Condon Principle

In 1925, before the development of the Schrödinger equation, Franck put forward qualitative arguments to explain the various types of intensity distributions found in vibronic transitions. His conclusions were based on the fact that an electronic transition in a molecule takes place much more rapidly than a vibrational motion of the nuclei that the instantaneous internuclear distance and the velocity of the nuclei can be considered remain unchanged during the electronic transition (later used as Born-Oppenheimer Approximation).

This means in the diagrams showing the potential energy curve of the two electronic states of the molecule, the transition must be represented by the vertical lines, i,e. the most probable or most intense transition will be those represented by the vertical lines.

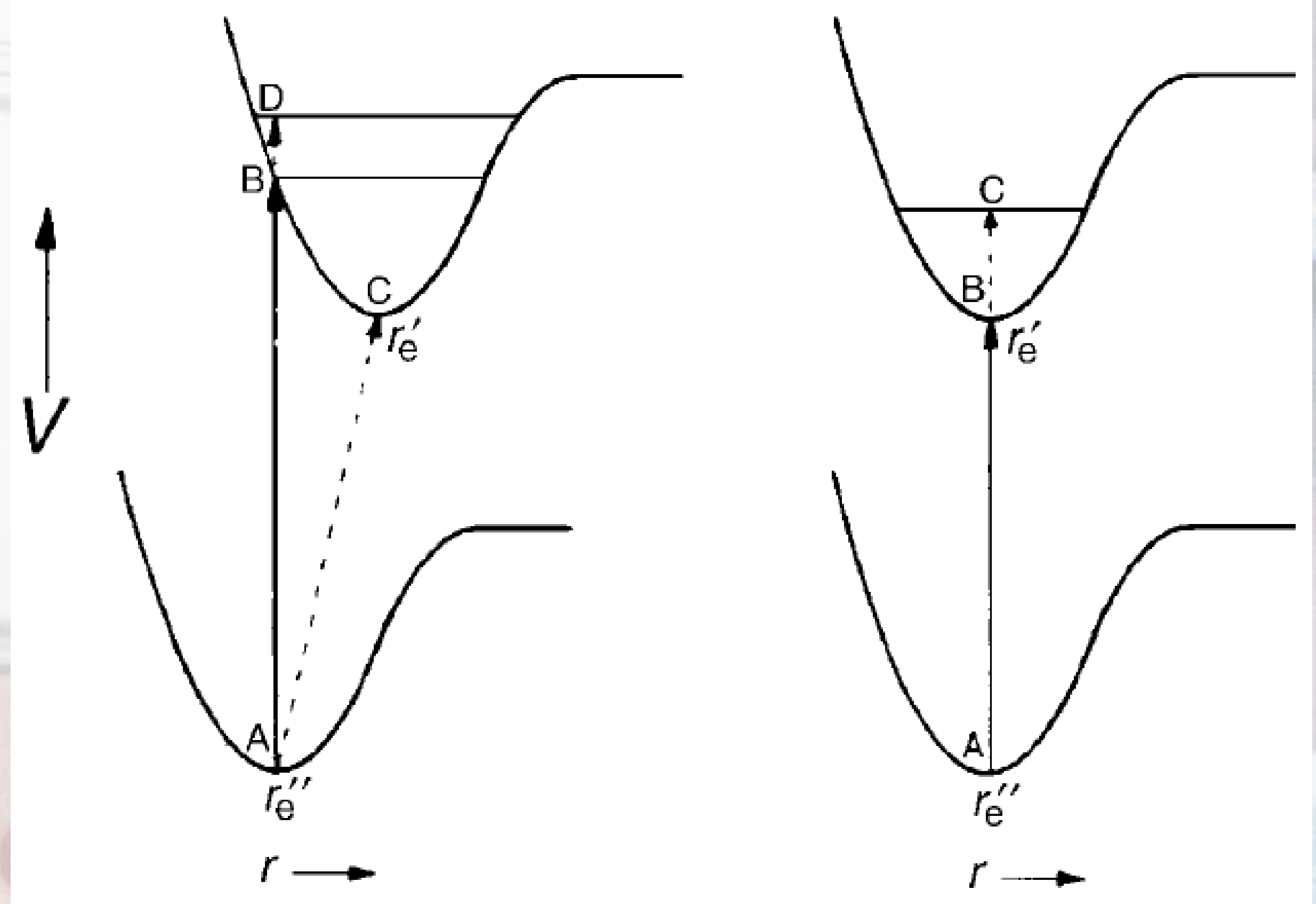
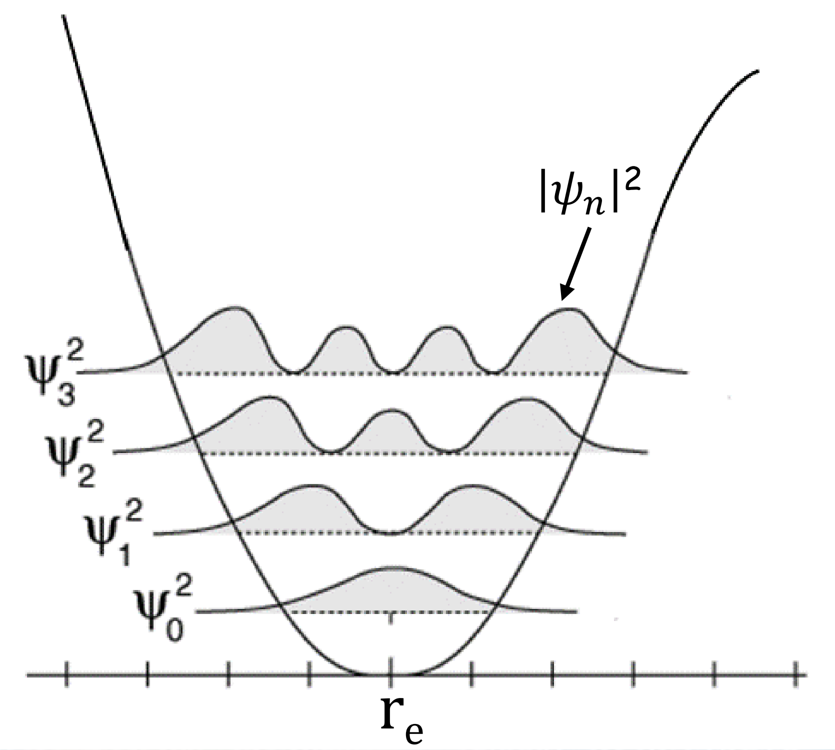


Figure demonstrating the Franck principle: for $r_e' > r_e''$ (left) and $r_e' = r_e''$ (right). The vibronic transition A → B is the most probable in both cases.

Another important factor to be considered is the distributions of the probability density $|\psi_n|^2$ in various vibrational level of each electronic states. The greater the values of $|\psi_n|^2$ at a particular values of internuclear distance r in a vibrational level, the greater the probability of the nuclei to be found at that distance apart. It is evident that $|\psi_n|^2$ is a maximum at the mid-point of the v = 0 level and near the turning points of the higher energy levels.



Accordingly, the Frack-Condon Principle is stated as **"The most probable vibrational transitions are those in which one of the two turning points of a vibrational level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of the level of other electronic state, except in case of v = 0 level for which the mid-point rather than the turning point must be substituted".**

QM formulation of Franck Condon Principle

In quantum mechanics, the intensity of a spectroscopic transition between two states of total wavefunction ψ' and ψ'' is dependent on the square of the corresponding transition moment R, given by

$$R = \int \psi'^{*} M \psi'' d\tau$$

where, M is the electric dipole moment having components $\sum e_i x_i$, etc. Ignoring the rotation and applying the Born-Oppenheimer approximation the total wavefunction may be written as:

$$\psi = \psi_e \psi_v$$

where, $\psi_e \; and \; \psi_v$ are the electronic and vibrational wavefunction, respectively. Further, the dipole moment M can also be written interms of electric and nuclear component as

$$M = M_e + M_n$$

Therefore, the transition moment for the two vibronic states is given by:

$$R = \int \psi'^*_e \psi'^*_v (M_e + M_v) \psi''_e \psi''_v d\tau_e d\tau_n$$

$$R = \int \psi'^*_e \psi'^*_v M_e \, \psi''_e \psi''_v d\tau_e dr + \int \psi'^*_e \psi'^*_v \, M_v \psi''_e \psi''_v d\tau_e dr$$

$d\tau_n$ is replaced by dr because vibrational (nuclear) wavefunction ψ_v depends on the internuclear distance r only.

Since, the nuclear dipole moment M_n is independent of the coordinates of the electrons (depend only on r), the second integral may be written as:

$$\int [\psi'^*_e \psi''_e d\tau_e] \psi'^*_v \, M_v \psi''_v dr$$

which is zero, because the electronic wavefunction belonging to different electronic states of a molecule are orthogonal $[\int \psi'^*_e \psi''_e d\tau_e = 0]$, hence;

$$R = \int \psi'^*_e \psi'^*_v M_e \, \psi''_e \psi''_v d\tau_e dr$$

$$R = \int \psi'^{*}_{e} M_e \, \psi''_{e} d\tau_e \int \psi'^{*}_{v} \psi''_{v} dr$$

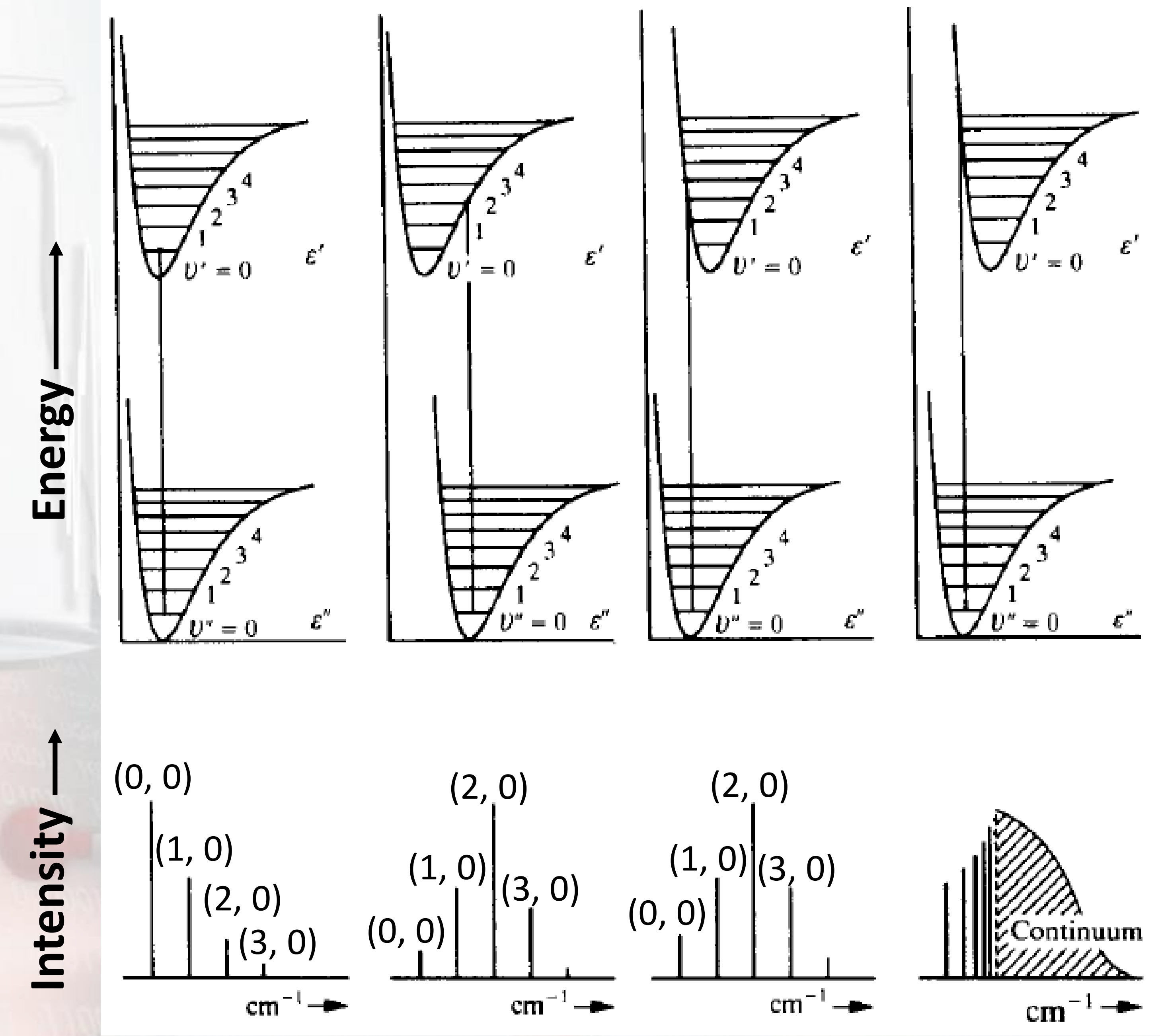
$$R^{v',v''} = R_e \int \psi'^{*}_{v} \psi''_{v} dr$$

where, R_e is electronic transition moment. As the variation of R_e with r is slow and therefore, R_e may be approximated as $\overline{R_e}$. Hence,

$$R^{v',v''} = \overline{R_e} \int \psi'^{*}_{v} \psi''_{v} dr$$

The average electronic transition moment $\overline{R_e}$, governs the intensity of the band-systems as a whole. The relative intensities of the various bands of the system mainly depends on the square of the overlap integral $\int \psi'^{*}_{v} \psi''_{v} dr$, which is the integral over the product of the vibrational wavefunction of the two combining states. It is known as "**Franck-Condon Factor**" $q^{v',v''}$;

$$q^{v',v''} = \left[\int \psi'^{*}_{v} \psi''_{v} dr \right]^2$$



$r_e' = r_e''$ O_2

$r_e' < r_e''$

$r_e' > r_e''$ CO

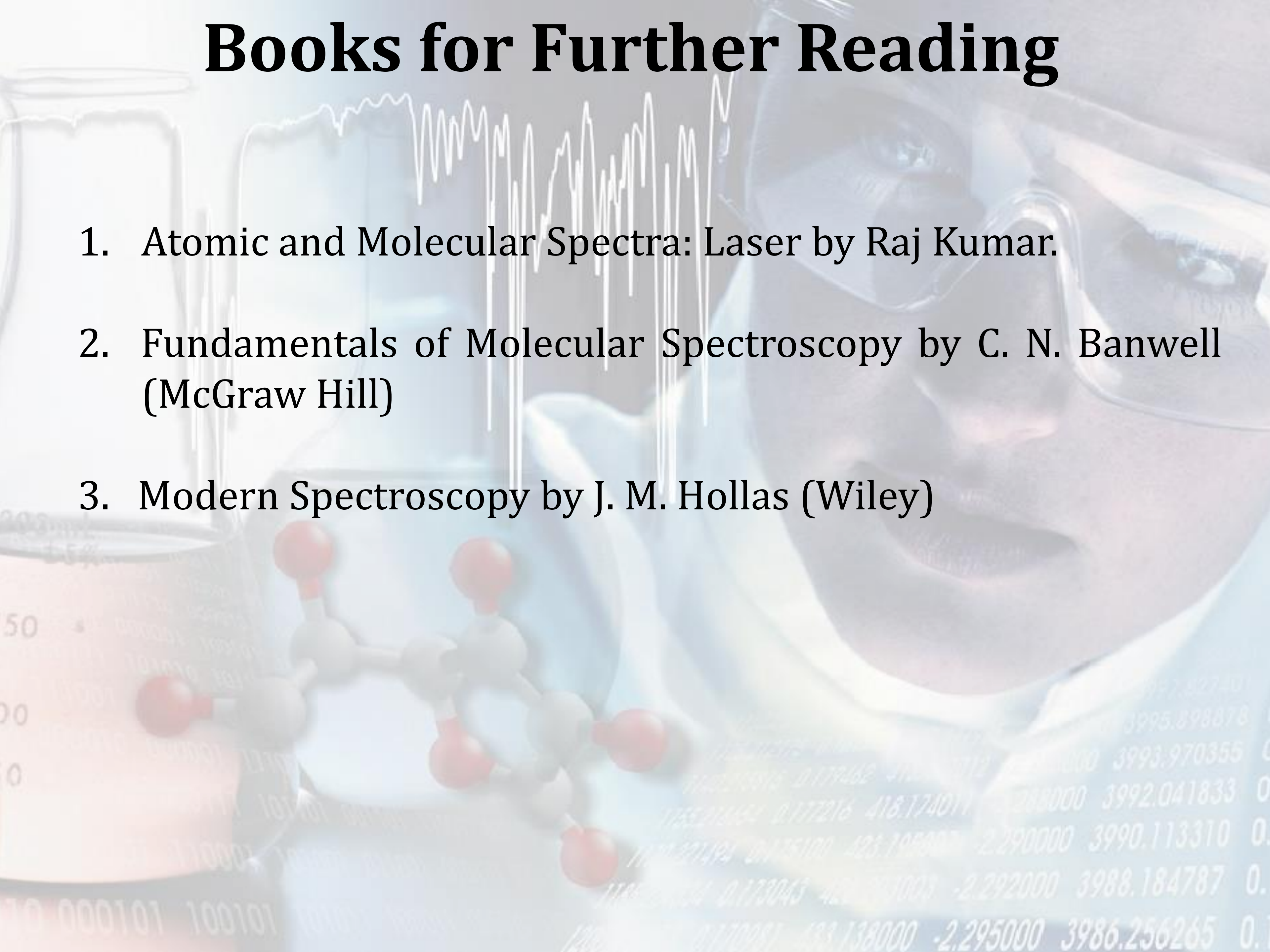
$r_e' \gg r_e''$ I_2

Case-I: When $r_e' = r_e''$, the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck-Condon principle suggests that a transition occurs vertically on this diagram, since the internuclear distance does not change. Thus the strongest spectral line of the v" = 0 progression will be the (0, 0). This observed in O_2 molecule.

Case-II: When $r_e' < r_e''$ or $r_e' > r_e''$, where the excited electronic state has a slightly smaller or larger internuclear separation than the ground state. A vertical transition from the v" = 0 level will be most likely to occur into the upper vibrational state v' = 2, transitions to lower and higher v' states being less likely; in general the upper state most probably reached will depend on the difference between the equilibrium separations in the lower and upper states. In case of CO molecule ($r_e' > r_e''$) this type of band-system is observed.

Case-III: When $r_e' \gg r_e''$, the upper state separation is drawn as considerably greater than that of the lower state. We see that, the vibrational level to which a vertical transition takes place has a high v' value, here transitions can occur to a state where the excited molecule has energy in excess of its own dissociation energy. From such states the molecule will dissociate without any vibrations and, since the atoms which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum is observed. This type of band-system is observed in I_2 Molecule.

Books for Further Reading



1. Atomic and Molecular Spectra: Laser by Raj Kumar.
2. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)
3. Modern Spectroscopy by J. M. Hollas (Wiley)

Thank you