

## VI. ELECTRONIC SPECTROSCOPY

The visible (V) and ultraviolet (UV) regions of the electromagnetic spectrum

Color	$\lambda/\text{nm}$	$\nu/10^{14}$ Hz	$E/\text{cm}^{-1}$	$E/\text{eV}$
vacuum ultraviolet	< 200			
ultraviolet	< 300	> 10	<50.000	
violet	420	7.1		2.9
blue	470	6.4	21.000	2.6
green	530	5.7		2.3
yellow	580	5.2		2.1
orange	620	4.8		2.0
red	700	4.3	14.000	1.8

A substance is colored if

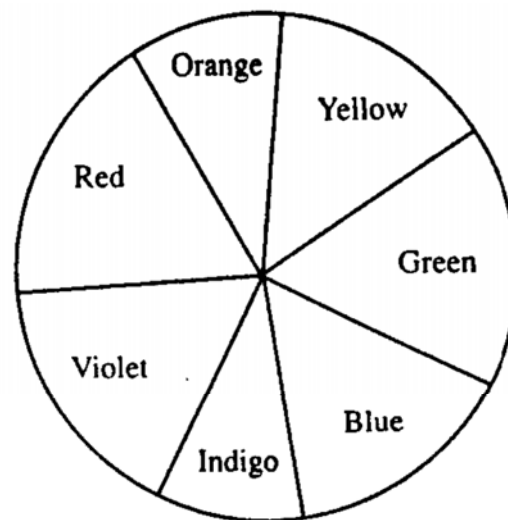
- it is able to absorb a band of wavelengths from incident white light;
- emission of particular frequencies of light from excited states;
- scattering of light of one frequency more favorably than light of another frequency (blue sky vs. red sky).

### Brief historical review

1666 (Sir Isaac Newton): during experiments with prisms he discovers that white light has components.

1800 (Sir William Herschel): discovery of the infrared radiation.

1801 (J. W. Ritter): discovery of the ultraviolet radiation.



**Fig. C.10** Newton's colour wheel. When light of a specific colour is absorbed from white light, the perceived colour is the one diametrically opposite across the wheel.

- 1801 (Thomas Young): discovery of optical interference (“*Whenever two portions of the same light arrive to the eye by different routes, either exactly or very nearly in the same direction, the light becomes most intense when the difference of the two routes is any multiple of a certain length, and least intense in the intermediate state of the interfering portions; and this length is different for light of different colours.*”)
- 1802 (W.H. Wollaston): repeats Newton’s prism experiments, but not with a round opening but with a slit. Discovers seven dark lines in the spectrum of the Sun.
- 1814-15 (Joseph von Fraunhofer): in front of the audience of the Munich Academy he presents his discovery of a large number of dark lines in the spectrum of the Sun. He names the lines according to the alphabet. Some of these names survive: we still talk about the *D* lines of sodium. The 350 lines presented are still called [Fraunhofer lines](#).
- 1858-59 (J. Plücker): investigates electric discharges in low pressure gases. He concludes that the spectra are determined by the gases, and the spectrum is independent from the metals used as electrodes.
- 1859-60 (Gustav Kirchhoff): show the equality of the absorption and emission rates. [For a given radiation (given wavelength, direction of propagation, and polarization) at a given temperature the capacity of any body to emit radiation divided by the absorption coefficient is the same, and it agrees with the capacity of emission of a black body by unit absorption coefficient.]

1860 (D. Brewster and J.H. Gladstone): identify about 8000 lines in the spectrum of the Sun. For some of them they show that they originate from the earth's atmosphere and erroneously conclude that all of the lines originate from there.

1879 (G.D. Living and James Dewar): observation of characteristic series in spectra (singlets, doublets, triplets). They also observe that in some series all members are sharp (s), while in some others all members are diffuse (d).

1885 (J.J. Balmer): provides a simple expression for all the lines in the spectrum of hydrogen, his formula is explained by Niels Bohr in 1913. The relation was given by Balmer for wavelengths, but we like wavenumbers better:

$$\lambda_n^{-1} = R \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \text{ where } R = 109\,677.58 \text{ cm}^{-1}$$

1890 (J.R. Rydberg): generalization of Balmer's formula:

$$\lambda_n^{-1} = \lambda_\infty^{-1} - \frac{R_\infty}{(n - \delta)^2},$$

where  $R_\infty = e^2 / 2a_0hc = 109\,737.32 \text{ cm}^{-1}$  is the Rydberg constant.

1896 (P. Zeeman): due to an external magnetic field, spectral lines split into components.

[Lorentz came up with a theory explaining this observation. He assumed that light is an isotropic harmonic oscillator (with mass  $m$  and charge  $e$ ) emitting radiation, the motion is governed by the magnetic force  $(e/c)\mathbf{v}\times\mathbf{B}$ .]

1900 (J.R. Rydberg): discovers that for a given element the wavenumber of all lines can be obtained as a difference of so-called term values. It was found in experiments that the wavenumber of the lines does not depend on whether it was observed in emission or absorption, and does not depend on the physical conditions either. However, intensity of the lines may strongly depend on the source conditions.

1900 (Max Planck): his work ends the classical period and starts “old quantum theory”.

### **Hallmarks of electronic spectroscopy**

- (1) Absorption bands of most solution phase spectra are so broad that the vibrational and rotational information is totally obscured.
- (2) In solid phase electronic excitation takes place in between bands, the information obtained has only limited utility for structure determinations.
- (3) Rotational fine structure is generally not resolved in the electronic spectra of polyatomic molecules.
- (4) While rotational (MW) and vibrational (IR, R) spectroscopies deal with transitions between energy levels within a single electronic potential well (PES), electronic spectroscopy deals with transitions of molecules between different electronic potential wells.

- (5) Electronic transitions may take place in a localized entity, such as a single atom, molecule, or a complex, or may be due to excitation of an electron across the band gap of a solid. A **chromophore** is a group of atoms that is responsible for the color of a molecule and which results in absorption in approximately the same spectral region whatever molecule it is in. Examples:  $\text{C}=\text{C}: \pi^* \leftarrow \pi$ ,  $\text{C}=\text{O}: \pi^* \leftarrow n$ .
- (6) Principles of laser action can be explained by using the terminology of electronic spectroscopy.
- (7) Once a molecule has absorbed a photon and finds itself in an excited electronic state, the excess energy can be eliminated, and the molecule returns to the ground state, by both **radiative** (emission of light: **fluorescence** and **phosphorescence**), and **non-radiative** [relaxation through collisions, thermal relaxation to states of intermediate energy, use of absorbed energy to promote chemical reaction, **internal conversion** (IC), **intersystem crossing** (ISC)] processes. The processes of radiative and non-radiative decay are conveniently illustrated on the **Jablonski diagram**:

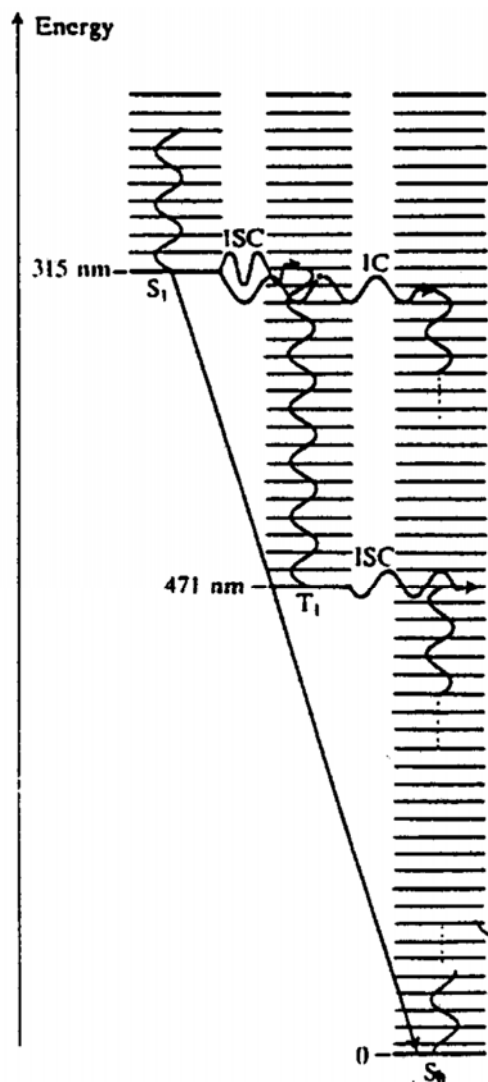


Fig. J.1 An example of a Jablonski diagram (for naphthalene).

A: absorption

F: fluorescence

P: phosphorescence

IC: internal conversion

ISC: intersystem crossing

R: (vibrational) relaxation

$S_0$ ,  $S_1$ : singlet electronic states

$T_1$ : lowest triplet excited electronic state



- (8) In photoelectron spectroscopy (PS) electrons are ejected from molecules by a high-energy photon; by measuring the kinetic energies of the photoelectron, the **orbital energies** of the molecule may be inferred.
- (9) Electronic absorption spectra may be used to provide information about the bonding characteristics of electronically excited molecules.
- (10) With a tunable laser (*e.g.*, dye laser) one can tune the laser frequency to a specific absorption frequency  $\rightarrow$  populate a single rovibrational (rovibronic  $\equiv$  rotational + vibrational + electronic) energy level of the excited electronic state  $\rightarrow$  resulting fluorescence emission spectrum is simple and straightforward to analyze.

## Intensity, oscillator strength

Lambert–Beer law:

$$I = I_0 \times 10^{-\varepsilon[c]\ell},$$

where  $\varepsilon$  is the **molar absorption coefficient**. The **integrated absorption coefficient** is defined as:

$$A := \int \varepsilon(\nu) d\nu.$$

Absorption characteristics of some groups and molecules:

Group	$\tilde{\nu}_{\max} / \text{cm}^{-1}$	$\lambda_{\max}/\text{nm}$	$\varepsilon_{\max}/\text{mol}^{-1}\text{cm}^{-1}$
C=C ( $\pi^*, \pi$ )	61.000	163	15.000
C=O ( $\pi^*, n$ )	36.000	280	10–20
H <sub>2</sub> O ( $\pi^*, n$ )	60.000	167	7.000

The integrated absorption coefficient is sometimes expressed in terms of the dimensionless oscillator strength,  $f$ :

$$f := \frac{4m_e c \varepsilon_0 \ln 10}{N_A e^2} \times A = 1.44 \times 10^{-19} \times A / (\text{cm}^2 \text{mmol}^{-1} \text{s}^{-1})$$

Thus, the oscillator strength of a transition is a measure of its intensity. It may be interpreted as the ratio of the observed intensity of radiation to the intensity of radiation absorbed or emitted by a harmonically bound electron in an atom (one bound to a nucleus by a Hooke's law force, and hence able to oscillate with simple harmonic motion in three dimensions); for such an electron  $f = 1$ . Typical  $f$  values:

Transition	$f$
Electric dipole allowed	$\approx 1$
Magnetic dipole allowed	$10^{-5}$
Electric quadrupole allowed	$10^{-7}$
Spin forbidden (S – T)	$10^{-5}$

If a transition has transition dipole moment  $\mu$  and it occurs at frequency  $\nu$ ,

$$f := \frac{8\pi^2 m_e \nu |\mu|^2}{3he^2} .$$

## Vibrational structure, Franck–Condon principle

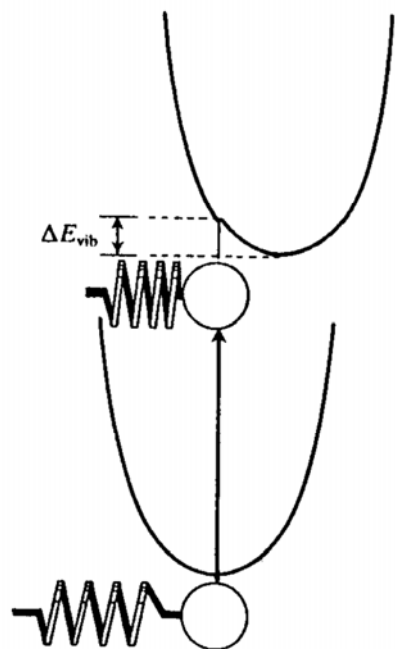
NB: The width of electronic absorption bands in liquid samples can be traced to the unresolved vibrational structure.

**Franck–Condon principle:** Because nuclei are much more massive than electrons, an electronic transition takes place while the nuclei in a molecule are effectively stationary. The principle thus governs the probabilities of transitions between the vibrational levels of different molecular electronic states.

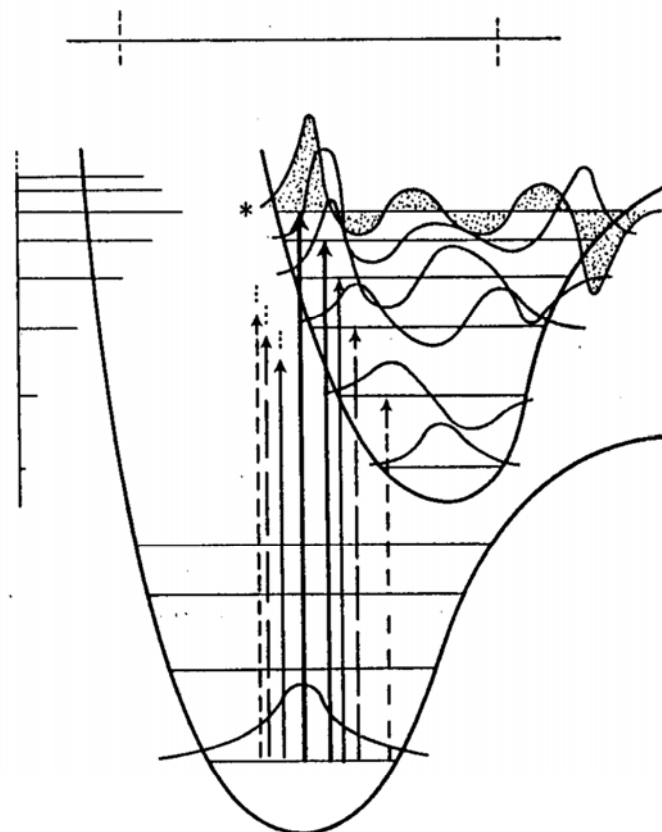
Designation of **vibronic** transitions:

$$I_{\nu}^{\nu'} \quad (\text{pl. } 1_0^1),$$

where  $I$  is the number of the normal vibration,  $\nu$  is the vibrational quantum number in the electronic ground state, and  $\nu'$  is the vibrational quantum number in the excited electronic state.



**Fig. F.8** The classical version of the Franck–Condon principle. The electronic transition from the lower parabola to the upper parabola occurs without change of nuclear position and without accelerating from rest. As a result, the nuclei are found in a stationary, high potential energy condition immediately after the transition. They respond by breaking into vibration. The vibrational energy of the upper state can be predicted by identifying the point at which the vertical line intersects the potential energy curve.



**Fig. F.9** The quantum mechanical version of the Franck–Condon principle. The most probable transition occurs from the initial ground state vibrational wavefunction to the vibrational state (\*) that it most resembles in the upper electronic state.

## Selection rules

The probability that a transition between two states will be induced by the oscillating electric field of a light wave is proportional to the square of the transition moment integral,  $M$ :

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

Divide  $\hat{\mu}$  into two components:

$$\hat{\mu} = \hat{\mu}_n + \hat{\mu}_e.$$

$$\psi = \psi_{es} \psi_v$$

$$\begin{aligned} M &= \int \psi_{e's'}^* \psi_{v'}^* (\hat{\mu}_n + \hat{\mu}_e) \psi_{es} \psi_v d\tau = \\ &= \int \psi_{e's'}^* \psi_{v'}^* \hat{\mu}_n \psi_{es} \psi_v d\tau + \int \psi_{e's'}^* \psi_{v'}^* \hat{\mu}_e \psi_{es} \psi_v d\tau = \\ &= \int \psi_{e's'}^* \psi_{es} d\tau_{es} \int \psi_{v'}^* \hat{\mu}_n \psi_v d\tau_v + \int \psi_{v'}^* \psi_v d\tau_v \int \psi_{e's'}^* \hat{\mu}_e \psi_{es} d\tau_{es} \end{aligned}$$

The first integral is zero, as the electronic states are mutually orthogonal to each other.

Thus, selection rules are determined by the following three integrals:

$$M = \int \psi_v^* \psi_v d\tau_n \int \psi_e^* \hat{\mu}_e \psi_e d\tau_e \int \psi_s^* \psi_s d\tau_s$$

First integral: **Franck-Condon factor** (FCF):

$$S_{v',v}^2 := \left[ \int \psi_v^* \psi_v d\tau_n \right]^2$$

Second integral: orbital selection rules

Third integral: spin selection rules

### *Spin selection rules*

A transition is spin allowed if and only if the **multiplicities** of the two states involved are identical (this follows from the orthogonality of spin wavefunctions). The spin selection rule is the strictest of selection rules governing electronic spectroscopy.

*Example:* singlet–triplet transition

$$\begin{aligned}
 \psi_s \psi_s d\tau &= \frac{1}{\sqrt{2}} \int_{e_{1,2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(1)\alpha(2)] d\tau_{s_{1,2}} = \\
 &= \frac{1}{\sqrt{2}} \left[ \int_{e_{1,2}} \alpha(1)\beta(2)\alpha(1)\alpha(2) d\tau_{s_{1,2}} - \int_{e_{1,2}} \beta(1)\alpha(2)\alpha(1)\alpha(2) d\tau_{s_{1,2}} \right] = \\
 &= \frac{1}{\sqrt{2}} \left[ \int_{e_1} \alpha(1)\alpha(1) d\tau_{s_1} \int_{e_2} \beta(2)\alpha(2) d\tau_{s_2} - \int_{e_1} \beta(1)\alpha(1) d\tau_{s_1} \int_{e_2} \alpha(2)\alpha(2) d\tau_{s_2} \right] = \\
 &= \frac{1}{\sqrt{2}} [(1)(0) - (0)(1)] = 0
 \end{aligned}$$

Thus, a singlet-triplet transition is spin forbidden.



### *Orbital selection rules*

An electronic transition is orbitally allowed if and only if the triple direct product  $\Gamma[\psi_{e'}] \otimes \Gamma[\mu_e] \otimes \Gamma[\psi_e]$  contains the totally symmetric irreducible representation of the point group of the molecule. The dipole moment operator once again has three components, which transform as  $x$ ,  $y$ , and  $z$ .

A transition which is both spin- and orbitally-allowed is called **fully allowed** and can be very intense. It should be immediately obvious that for a totally symmetric ground state, only transitions to excited states which have the same symmetry as at least one of the components of the dipole moment operator will be orbitally-allowed.

*Example:*  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  spin-allowed electronic transition in benzene

The dipole moment operator transforms as  $a_{2u}(z) \oplus e_{1u}(x, y)$ . Thus,

$$A_{1g} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} B_{2u} = \begin{pmatrix} b_{1g} \\ e_{2g} \end{pmatrix},$$

*i.e.*, the transition is orbitally forbidden. Such spin-allowed but orbitally-forbidden transitions exhibit intensities between those of fully allowed and spin-forbidden transitions.

### *Vibronic selection rules*

The transition dipole moment can be written as

$$M = \int \psi_e^* \psi_v^* \hat{\mu} \psi_e \psi_v d\tau_{\text{en}} \int \psi_s^* \psi_s d\tau_s .$$

In the preceding discussion of orbital selection rules we have implicitly considered only 0–0 (“pure electronic”) transitions, for which both for the ground and the excited electronic states the vibrational part of the wavefunctions are totally symmetric. The condition for a vibronic transition to be allowed is that the integral

$$\int \psi_e^* \psi_v^* \hat{\mu} \psi_e \psi_v d\tau_{\text{en}}$$

be nonzero.

*Example 1:* *p*-difluorobenzene,  $D_{2h}$  point-group symmetry.

Question: is the spin-allowed pure electronic transition  ${}^1B_{2u} \leftarrow {}^1A_g$  of *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> orbitally allowed?

(a) Pure (0–0) electronic transition:

$$\text{dipole moment: } b_{3u}(x) \oplus b_{2u}(y) \oplus b_{1u}(z), \quad B_{2u} \begin{pmatrix} b_{3u} \\ b_{2u} \\ b_{1u} \end{pmatrix} A_g = \begin{pmatrix} b_{1g} \\ a_g \\ b_{3g} \end{pmatrix} \Rightarrow \text{allowed}$$

vibronic transition:

$$B_{2u} a_g \begin{pmatrix} b_{3u} \\ b_{2u} \\ b_{1u} \end{pmatrix} A_g a_g = \begin{pmatrix} b_{1g} \\ a_g \\ b_{3g} \end{pmatrix} \Rightarrow \text{allowed}$$

This transition moment integral also tells us that the transition is y-polarized.

$$(b) \text{ Transition } 8_0^1: B_{2u} b_{2g} \begin{pmatrix} b_{3u} \\ b_{2u} \\ b_{1u} \end{pmatrix} A_g a_g = \begin{pmatrix} b_{3g} \\ b_{2g} \\ b_{1g} \end{pmatrix} \Rightarrow \text{forbidden}$$

$$(c) \text{ Transitions } 7_0^1 \text{ and } 7_1^0: \text{ fully allowed, } x\text{-polarized, } B_{2u} a_g \begin{pmatrix} b_{3u} \\ b_{2u} \\ b_{1u} \end{pmatrix} A_g b_{1g} = \begin{pmatrix} a_g \\ b_{1g} \\ b_{2g} \end{pmatrix} \Rightarrow \text{allowed}$$

Example 2:  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  of benzene  $\left[ (a_{2u})^2 (e_{1g})^4 \rightarrow (a_{2u})^2 (e_{1g})^3 (e_{2u})^1 \right]$

(a) 0–0 transition:  $B_{2u} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} A_{1g} = \begin{pmatrix} b_{1g} \\ e_{2g} \end{pmatrix} \Rightarrow$  forbidden

(b)  $\nu_{10}(e_{2g})$  transition ( $10_0^1$ ):

$$B_{2u} e_{2g} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} A_{1g} a_{1g} = e_{1u} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} a_{1g} = \begin{pmatrix} e_{1g} \\ a_{1g} \oplus a_{2g} \oplus e_{2g} \end{pmatrix} \Rightarrow \text{allowed}$$

Thus, by coupling an orbitally-forbidden electronic transition with a vibrational transition, it is possible that the selection rules can be satisfied and some intensity can be expected.

### Intensities of electronic transitions

Governing condition	Range of $\varepsilon$ values ( $\text{mol}^{-1} \text{cm}^{-1}$ )
spin-forbidden (strict!)	$10^{-5} - 10^0$
spin-allowed, orbitally forbidden	$10^0 - 10^3$
fully allowed	$10^3 - 10^5$

NB1: The vibrational structure of the spectrum depends on the relative displacement of the two potential energy curves, and a long **progression** of vibrations is stimulated if the two states are appreciably displaced.

NB2: The separation of the vibrational lines of an electronic absorption spectrum depends on the vibrational energies of the upper electronic state. Hence electronic absorption spectra may be used to assess the force fields and dissociation energies of electronically excited molecules.

## Fates of electronically excited states

*Radiative decay* → excited molecule discards its excitation energy as a photon:

- fluorescence
- phosphorescence

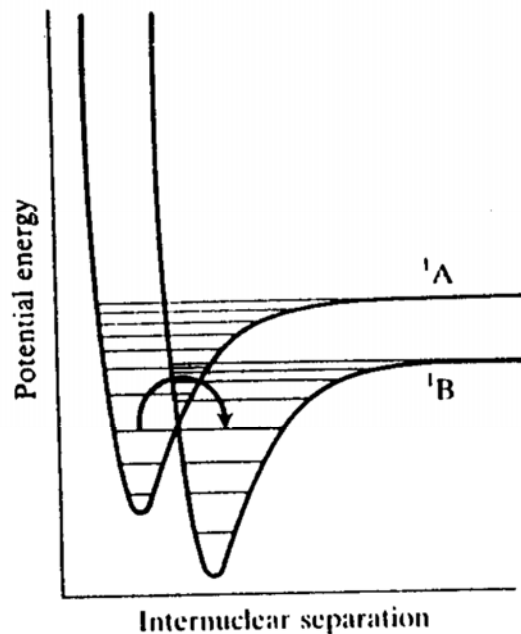
*Nonradiative decay* → excess energy is transferred into the vibration, rotation, and translation of the surrounding molecules:

- thermal degradation
- chemical reaction
- dissociation, predissociation
- internal conversion, IC
- intersystem crossing, ISC

NB1: IC is generic term for spin-allowed non-radiative electronic-state changes.

NB2: ISC is a generic term for spin-forbidden non-radiative electronic-state changes.

## Internal conversion (IC)



**Fig. 1.5** In an internal conversion, a molecule makes a non-radiative transition from one electronic state to another of the same multiplicity. The transition occurs between vibrational states close to the point of intersection of the two molecular potential energy curves.

In an IC, a molecule makes a non-radiative transition from one electronic state to another of the same multiplicity. The transition occurs between vibrational states close to the point of intersection of the two molecular potential energy curves.

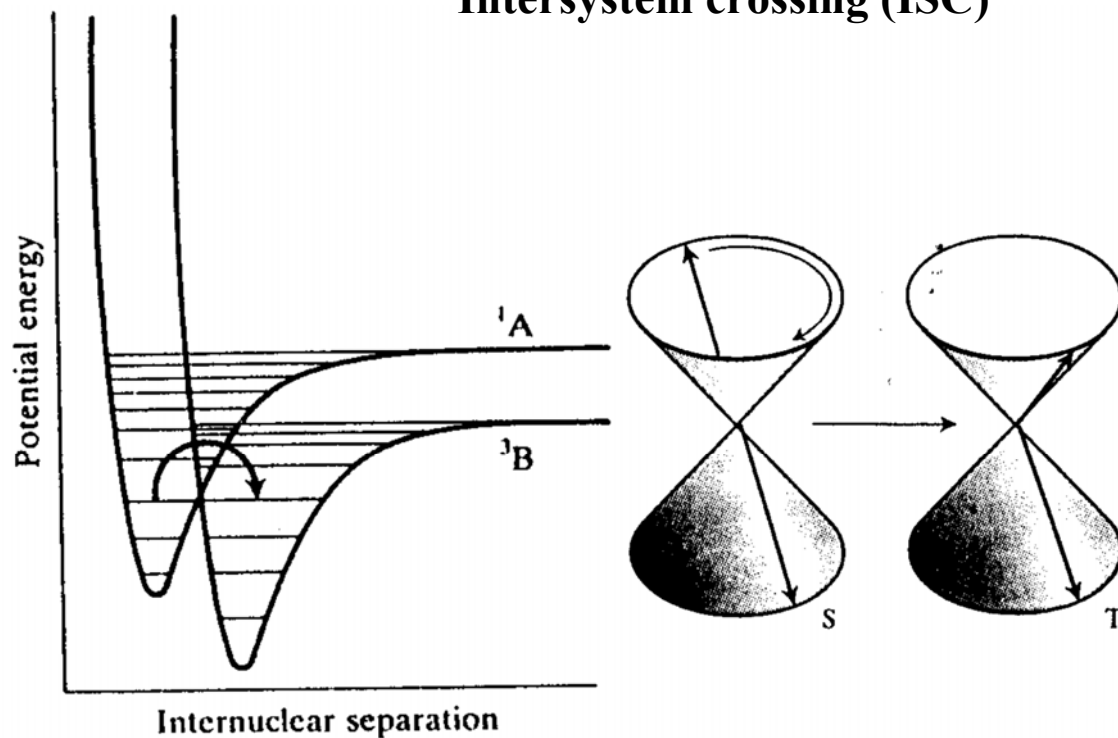
Two states of the same energy are mixed strongly if a perturbation is present, and hence the initial state can be nudged into the final state by even a weak perturbation. The perturbation that drives IC is the breakdown of the BO approximation, for the electrons do not exactly follow the changing location of the nuclei.

*Classical interpretation:* the intersection of the potential energy curves marks the point at which the nuclei have the same locations in the two states + stationary. Hence a molecule in state A may swing up to its turning point, where a perturbation flips it into state B with a different arrangement of electrons (and hence with the nuclei experiencing a different force field) but the same arrangement of the nuclei. When the molecule resumes its oscillation it finds itself in the potential well corresponding to state B.

*Quantum mechanical interpretation:* the vibrational wavefunction of the two electronic states resemble each other most closely (in the sense of having the greatest overlap) in the states that occur close to the intersection. For these states, the dynamical state of the nuclei in state B resembles that of the nuclei in state A most closely.



## Intersystem crossing (ISC)

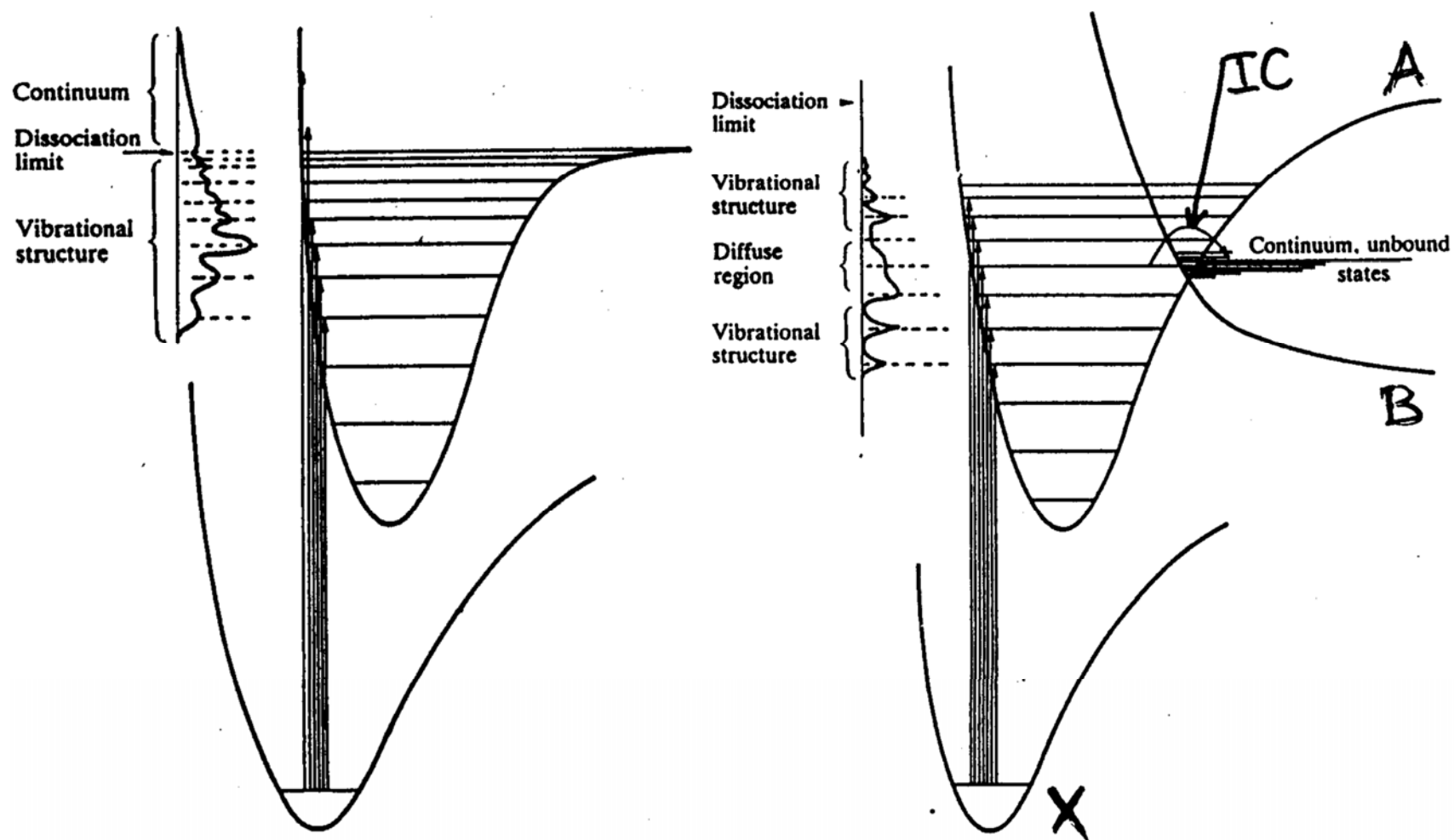


**Fig. 1.6** In an intersystem crossing, a molecule makes a non-radiative transition from one electronic state to another of a different multiplicity (here, from singlet to triplet). The transition occurs between vibrational states close to the intersection of the two molecular potential energy curves.

**Fig. 1.7** Intersystem crossing involves the relative reorientation of electron spins within the molecule. This illustration shows the relative reorientation required if a singlet state is to convert into the  $M_S=0$  component of the triplet. (Different relative motions result in crossing into the  $M_S=\pm 1$  components; see "singlet and triplet states.")

To achieve the conversion of a singlet state into a triple state it is necessary to change the relative orientation of the spins of the two electrons. A field from a laboratory magnet cannot cause ISC (unless the two electrons have different *g*-factors) because it is homogeneous on a molecular scale, affects both spins equally, and cannot twist one spin relative to the other. However, a magnetic field from within a molecule may be able to rephase the spins. For example, the *spin-orbit coupling* experienced by two electrons may differ if they are in different parts of a molecule, and the different local magnetic fields result in the realignment of the two spins. This is the reason why molecules containing heavy atoms, with large spin-orbit couplings, undergo efficient ISC (see phosphorescence).

## Dissociation, predissociation



The onset of **dissociation** can be detected in an absorption spectrum by seeing that the vibrational structure of a band terminates at a certain energy. Absorption occurs in a continuous band above this dissociation limit because the final state is an unquantized translational motion of the fragments.

In some cases the vibrational structure disappears but resumes at higher photon energies. This **predissociation** can be interpreted in terms of crossings of the potential energy curves. Thus, predissociation is dissociation that occurs in a transition before the dissociation limit is attained. **Induced predissociation** is predissociation that is induced by some external influence, such as collisions or an applied field.

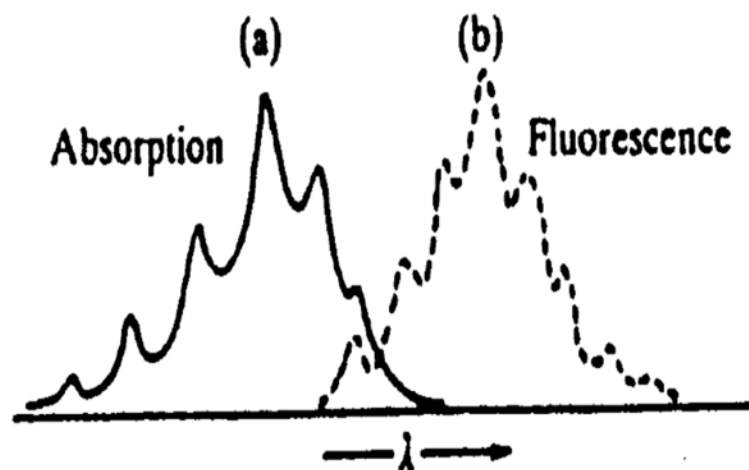
## Fluorescence

Light emitted from an excited molecule is called fluorescence if the emission mechanism does not require the molecule to pass through a state of different spin multiplicity from that of the initial state. Fluorescence generally ceases almost immediately after the exciting radiation is removed.

Characteristics:

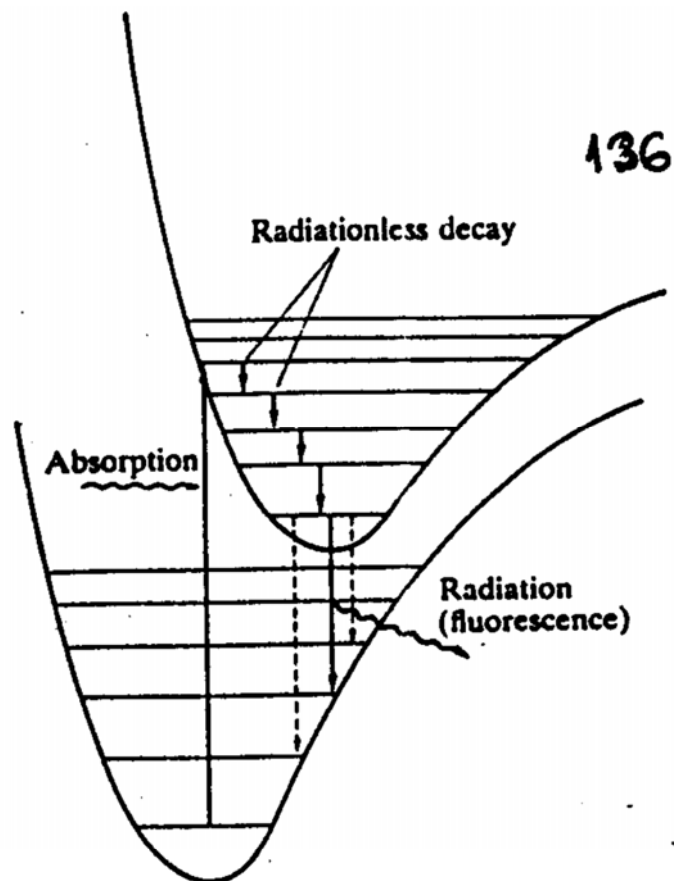
- ◆ in normal fluorescence the emission is spontaneous
- ◆ the fluorescence should appear at lower frequency (higher wavelength) than the incident light
- ◆ there may be vibrational structure in the fluorescence spectrum, the spectrum of radiation emitted on the decay of the ground vibrational state of the upper electronic state into different vibrational levels of the lower electronic state; examination of this vibrational structure can provide information about the force constants of the molecule in its ground state (this is in contrast to electronic absorption spectra, which provide information about force constants of bonds in the upper electronic state)

- ◆ fluorescence spectra may resemble the mirror image of absorption spectra



**Fig. 17.10** The absorption spectrum (a) shows a vibrational structure characteristic of the upper state. The fluorescence spectrum (b) shows a structure characteristic of the lower state; it is also displaced to lower frequencies (but the 0-0 transitions are coincident) and resembles a mirror image of the absorption.

- ◆ Kasha's law: the fluorescent level is the lowest level of the specified multiplicity ( $S_1$  rather than  $S_2$  or above); thus, if the initial absorption is not to the lowest excited state of the molecule, internal conversion (IC) occurs in which collisions cause the higher states to make a radiationless transition into the lowest excited state of the given multiplicity
- ◆ whether or not fluorescence occurs depends on a competition between radiative emission and the radiationless de-excitation by energy transfer to the surrounding medium (the solvent can carry away the electronic excitation energy if its molecules have energy levels that match the energy of the excited molecule)



**Fig. 17.9** The sequence of steps leading to fluorescence. After the initial absorption the upper vibrational states undergo radiationless decay by giving up energy to the surroundings. A radiative transition then occurs from the ground state of the upper electronic state. (In practice the separation of the curves is 10 to 100 times greater than the separation of the vibrational levels.)



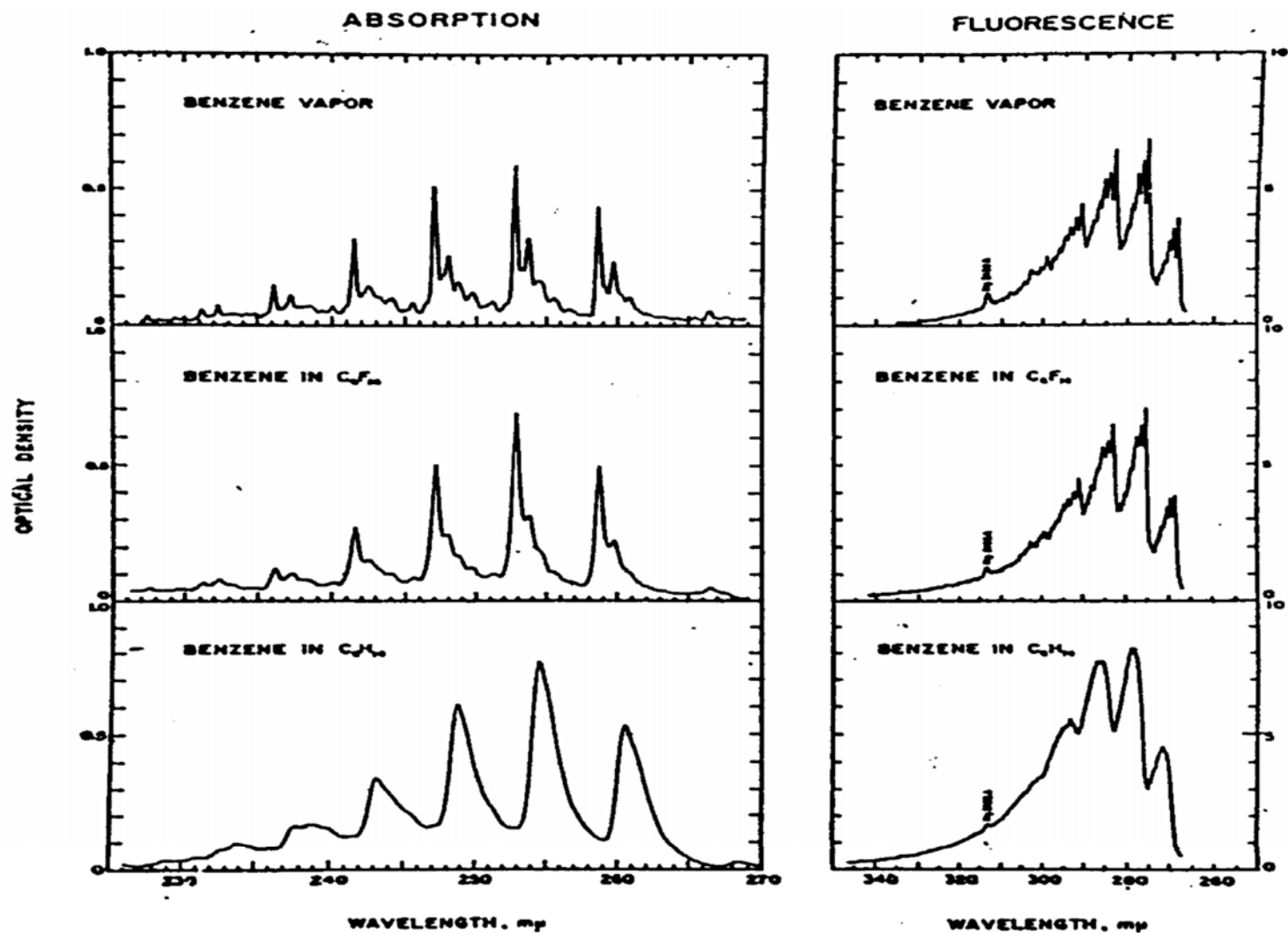


Figure 7.12  $S_1 \leftarrow S_0$  absorption spectra of benzene between 2300 and 2700 Å in the vapor, in  $C_6F_{14}$ , and in  $C_6H_{14}$ . Used with permission from C. W. Lawson, F. Hirayama, and S. Lipsky, *J. Chem. Phys.* 51: 1595 (1961).

## Phosphorescence

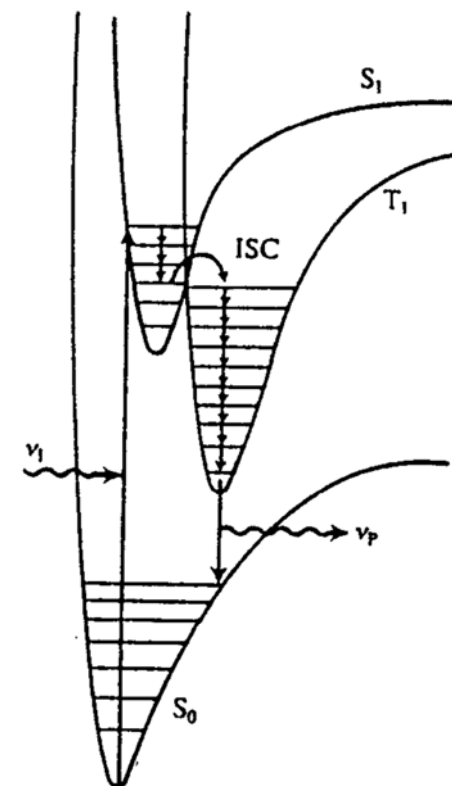
When a phosphorescent material is illuminated, it emits radiation that may persist for an appreciable time after the stimulating illumination has been removed. The fundamental distinction between phosphorescence and fluorescence is that the former involves a change in the multiplicity of the excited state but the latter does not.

Phosphorescence may occur if

- ◆ there is a suitable triple state in the vicinity of the excited singlet states;
- ◆ sufficiently strong **spin-orbit coupling** to induce ISC (in the heavy atom effect ISC is enhanced by that atom's SO coupling);
- ◆ must be enough time for the molecule to cross from one curve to the other, which means that vibrational deactivation must not proceed so fast that the molecule is quenched and taken below that point where the curves intersect before ISC has time to occur.

Mechanism:

- (a)  $S_1 \leftarrow S_0$  excitation
- (b) non-radiative vibrational energy loss
- (c) ISC ( $T_1 \leftarrow S_1$ )
- (d) non-radiative vibrational energy loss
- (e)  $S_0 \leftarrow T_1$  phosphorescence



**Fig. P.13** The mechanism of phosphorescence. Absorption take the molecule to the excited singlet state; as its vibrational excitation is discarded it undergoes an intersystem crossing into a triplet state. Nonradiative vibrational relaxation continues, to leave the molecule trapped in the triplet state. However, it can undergo a weak radiative transition to the ground singlet state because the selection rules are broken by the spin-orbit coupling.

## Photoelectron Spectroscopy (PS)

In PS electrons are ejected from molecules by a high-energy photon ( $M + h\nu \rightarrow M^+ + e^-$ ). The kinetic energy of the emitted photoelectron is the energy of the incident photon,  $h\nu$ , less the ionization energy of the photoelectron ( $IE_k$ , the  $k$ th bonding energy):

$$h\nu = IE_k + E_k .$$

The energy of the emitted photoelectron:

$$E_k = \frac{1}{2} m_e v_k^2 = h\nu - IE_k .$$

Refinements of the simple picture:

- (a) a photoelectron may originate from a number of different orbitals, hence a series of different kinetic energies of the photoelectrons will be obtained;
- (b) the ejection of an electron may leave an ion in a vibrationally excited state. Each vibrational quantum that is excited leads to a different kinetic energy of the photoelectron, and gives rise to the fine structure in the PS spectrum;
- (c)  $IE_1$  is the smallest amount of energy which needs to be invested to photoionize a molecule (1.5 eV for metals, 5–15 eV for isolated molecules).

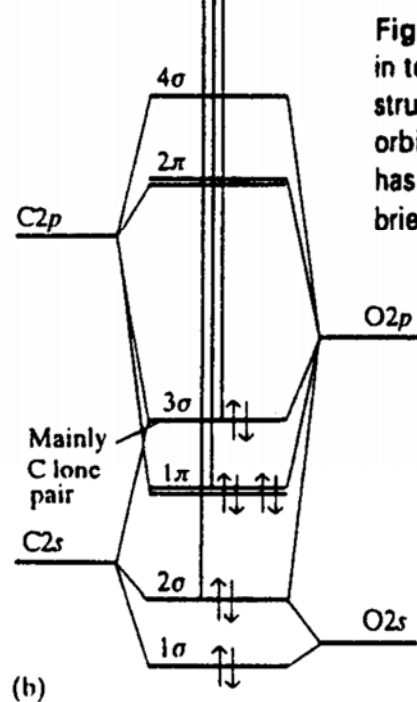
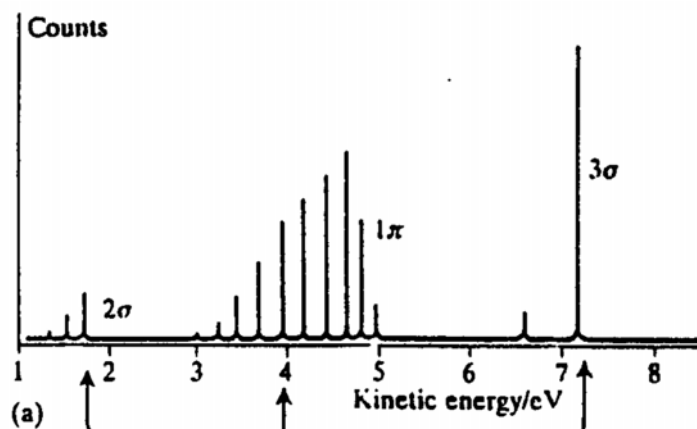


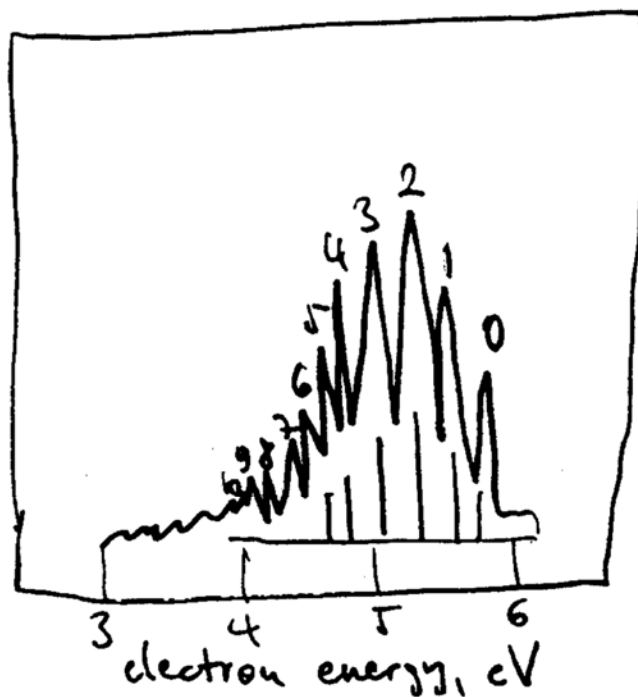
Fig. P.14 The uv-photoelectron spectrum of carbon monoxide and its interpretation in terms of the molecular orbital energy level diagram. Note the extensive vibrational structure when the photoelectron is ejected from the  $2p\pi$  bonding orbital. The  $2p\sigma$  orbital is largely nonbonding on the carbon atom, and loss of an electron from it has little effect on the force field; hence the vibrational structure of the band is very brief.

Briefly, the PS spectrum from the valence region reflects the higher MO levels in the **MO diagram**.

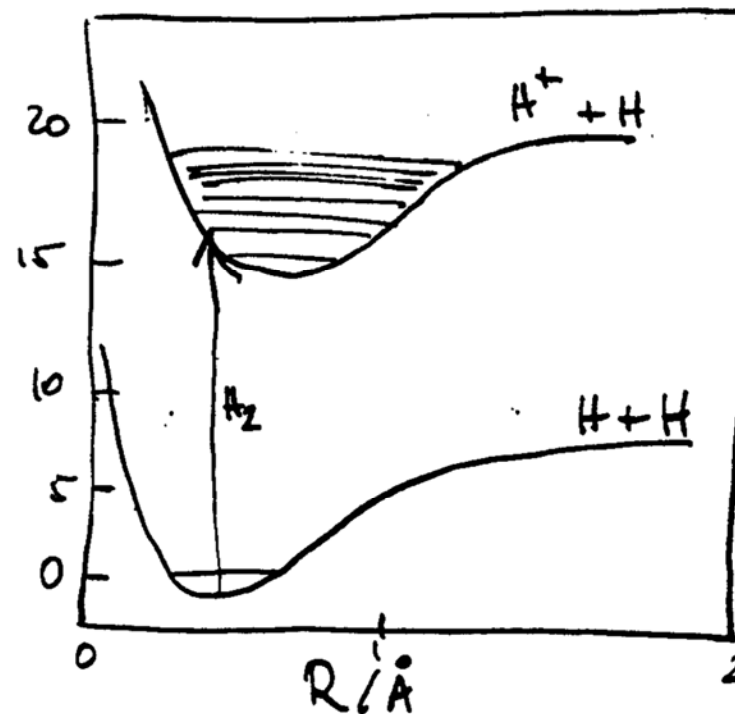
Photoelectron spectroscopy working with UV photon is called UV-photoelectron-spectroscopy (**UPS**). When X-rays are used for the photoionization, we speak about **XPS** (the old name of the technique is **ESCA**, Electron Spectroscopy for Chemical Analysis).

The most commonly used source of UV photons is a helium gas discharge tube, the most intense line has a wavelength of 58.4 nm and an energy of 21.22 eV. This is the so-called **He(I) line**. Occasionally the **He(II) line** ( $h\nu = 40.8$  eV) is also employed, corresponding to the emission of a singly ionized He atom.

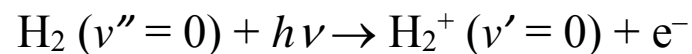
PES spectrum of  $\text{H}_2$  gas  
excited by He (21.22 eV)



Potential energies of  $\text{H}_2$   
and  $\text{H}_2^+$



The highest-energy electrons emitted by the sample (line labelled 0) come from the production of  $\text{H}_2^+$  ions in their ground vibrational state ( $\nu = 0$ ):



The electrons emitted in this peak have an energy of 5.77 eV, so that  $E(\text{M}^+) - E(\text{M})$  for the  $v = 0$  transition is  $21.22 - 5.77 = 15.45$  eV, which is the **adiabatic ionization potential** for the hydrogen gas.

The Franck-Condon principle leads us to expect that the 0–0 transition will not be the most probable. The energy difference for the strongest band (in this case  $v = 0 \rightarrow 2$ ) is referred to as the **vertical ionization potential**; this ionization potential for  $\text{H}_2$  is  $21.22 - 5.24 = 15.98$  eV, about 0.5 eV ( $4000 \text{ cm}^{-1}$ ) larger than the adiabatic ionization potential.



## **XPS $\equiv$ ESCA**

When the radiation source is in the X-ray region, each photon carries sufficient energy to eject electrons from atomic cores. This technique is known as XPS or ESCA, Electron Spectroscopy for Chemical Analysis. Why ESCA (note, at the same time, that the name ESCA covers several other electronic spectroscopy techniques, like Auger-spectroscopy)? The “inner energies” (energies of inner electron orbitals) are largely independent of the state of chemical bonding of the atom, so XPS spectra can be used to identify the elements present. Note, however, that binding energies of core electrons depend slightly on the chemical environment of the atom  $\rightarrow$  “chemical shifts”. These chemical shifts offer the possibility of obtaining structural information. For example, the nitrogen 1s spectrum  $\text{Na}^+\text{N}_3^-$  shows two peaks with relative intensities of 2:1, indicating that the three N atoms are not chemically equivalent.

## Theoretical (quantum chemical) computations

Molecular electronic spectroscopy can provide information on:

- rotational parameters (moments of inertia and therefore molecular geometries)
- vibrational parameters (frequencies and force constants)
- electronic excitation energies (important for photochemical reactions, like photosynthesis)
- electronic excitation energies (important for photochemical reactions, like photosynthesis)
- ionization potentials
- dissociation energies for ground and excited electronic states

Theoretical computation of excited-state wavefunctions is quite difficult due, for example, to open-shell configurations, configuration interaction (CI) is generally considerably more important than for closed-shell systems.

### Koopmans' theorem (1933)

According to Koopmans' theorem (Koopmans' principle) for a neutral molecule the following relation holds approximately for the  $k$ th ionization energy,  $I_k$ : Hartree–Fock (HF, SCF) pályae energiák ellentettjével:

$$I_k = -\varepsilon_k^{\text{SCF}},$$

where  $\varepsilon_k^{\text{SCF}}$  is the canonical orbital energy of a bound MO, where  $k = 1$  for the highest occupied molecular orbitals (HOMO),  $k = 2$  for the next-to-the-highest, etc.

This “theorem” is just an approximate one, as it considers neither the electronic rearrangement (relaxation) following an ionization, nor the known shortcomings of the HF model (most importantly the lack of electron correlation). Fortunately, the error introduced by these two approximations is about the same magnitude but opposite in sign, yielding the approximate validity of the Koopmans' principle.

## Ionization potentials (IP)

### H<sub>2</sub>O lowest IP (eV)

Koopmans	0.507
CISD (H <sub>2</sub> O – H <sub>2</sub> O <sup>+</sup> )	0.452
Experiment	0.463

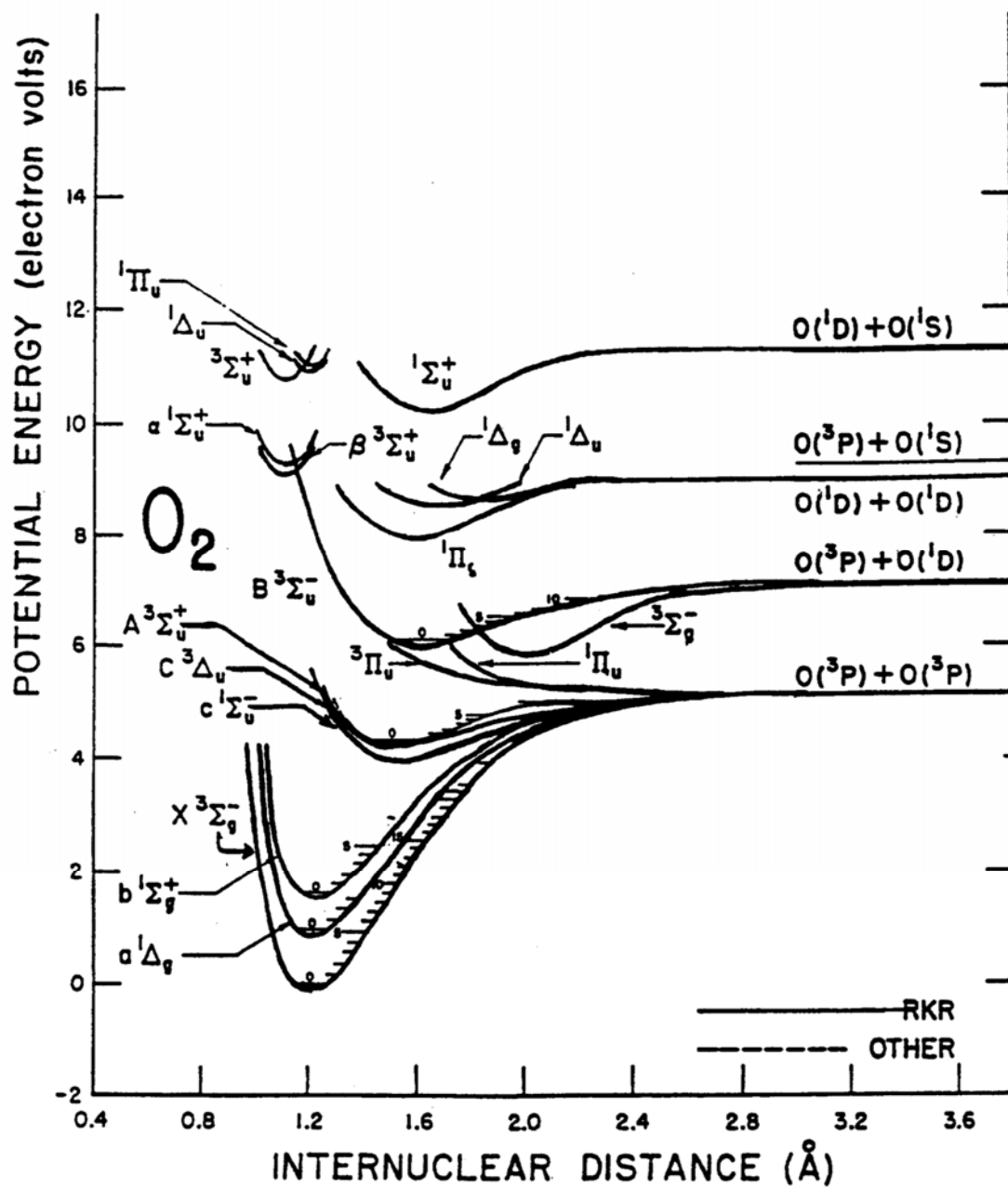
### N<sub>2</sub>

Orbital	Koopmans	CISD (N <sub>2</sub> – N <sub>2</sub> <sup>+</sup> )	Experiment
3σ <sub>g</sub>	0.635	0.580	0.573
1π <sub>u</sub>	0.615	0.610	0.624

$^{16}\text{O}_2$ 

State	$T_e/\text{cm}^{-1}$	$\omega_e/\text{cm}^{-1}$	$\omega_e x_e/\text{cm}^{-1}$	$B_e/\text{cm}^{-1}$	$\alpha_e/\text{cm}^{-1}$	$R_e/\text{\AA}$
B $^3\Sigma_u^-$	49 802	700.4	8.002	0.819	0.011	1.60
A $^3\Sigma_u^+$	36 096	819.0	22.5	1.05	–	1.42
b $^1\Sigma_g^+$	13 195	1432.7	133.95	1.4004	0.01817	1.22675
a $^1\Delta_g$	7 918	1509.3	12.9	1.4264	0.0171	1.2155
X $^3\Sigma_g^-$	0	1580.4	12.073	1.4457	0.0158	1.2074

P.H. Krupenie, *J. Phys. Chem. Ref. Data* 1, 423 (1972)

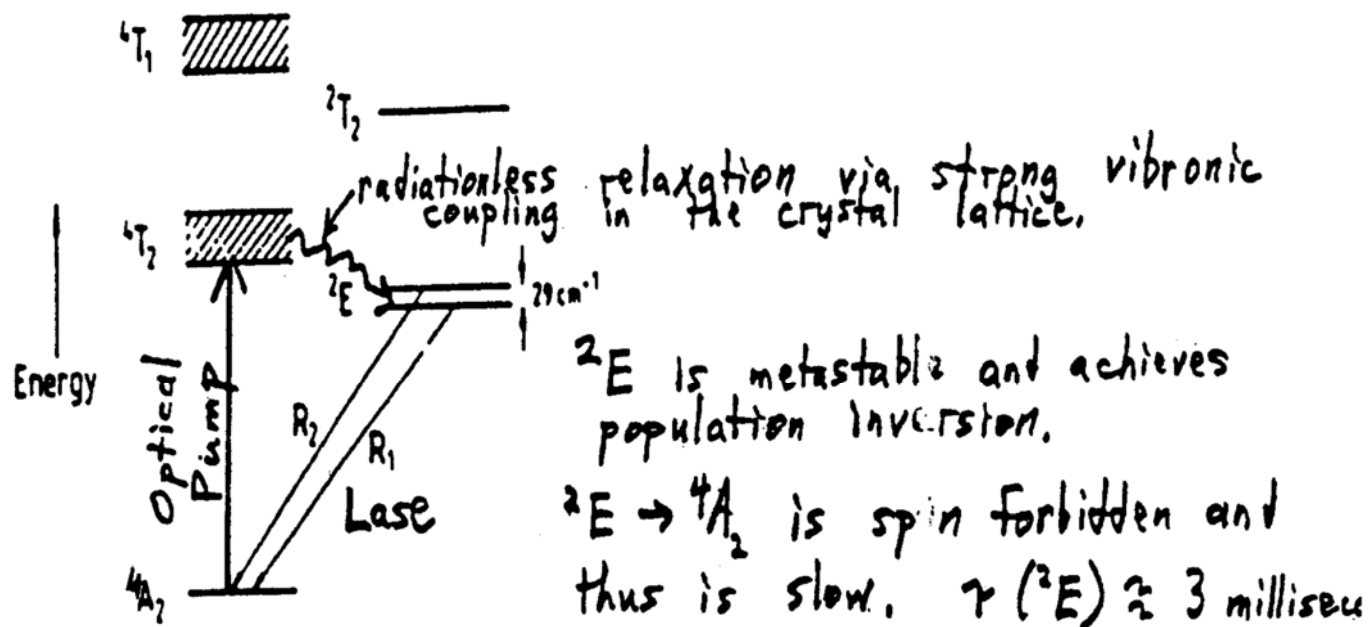


## Lasers I. The ruby pulsed laser

The first laser was the ruby laser, built by Maiman in CA, USA in 1960. Townes had built a maser in 1954, and Townes and Schawlow had described conditions for constructing lasers in 1958.

Ruby rod –  $\text{Al}_2\text{O}_3$  crystals with 1% of  $\text{Al}^{3+}$  replaced with  $\text{Cr}^{3+}$ . A reflective surface is placed at the end of the rods. Pumping is achieved with a flashlamp.

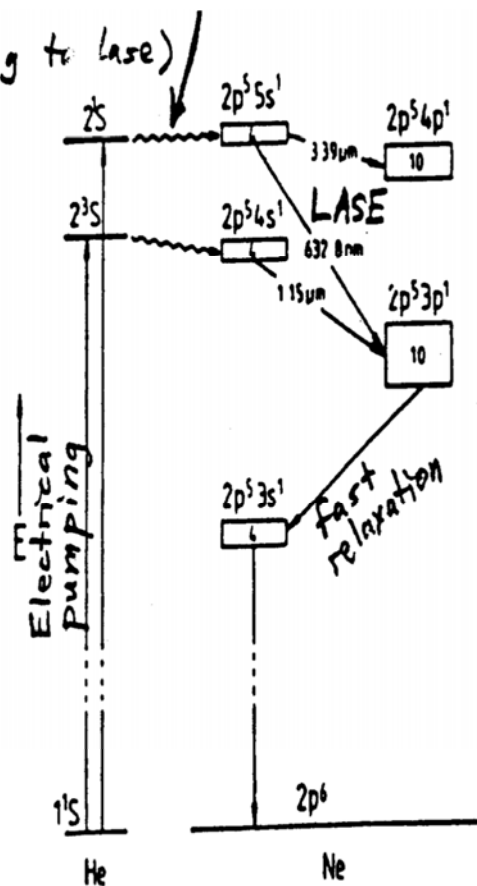
( $\text{Cr}^{3+}$  energy levels)



## Lasers II. The He-Ne CW gas laser

Gas bulb with 1 torr He, 0.1 torr Ne. Electrical pumping of He with  $e^-$  collisions in a discharge between electrodes.  $\text{He}^* + \text{Ne} \rightarrow \text{He} + \text{Ne}^*$  is the energy transfer mechanism.

$$\tau(2^3S \text{ He}) = 8000 \text{ s} \quad (\text{too long to lase})$$



Ne lifetimes

$$\tau(2p^5 4s^1) = 100 \text{ ns}$$

$$\tau(2p^5 3p^1) = 10 \text{ ns}$$

well suited for  
laser action)

Figure 9.12 Energy levels of the He and Ne atoms relevant to the helium–neon laser. The number of states arising from each Ne configuration is given in a ‘box’.