

Chapter 16

Emission Spectroscopy

General bibliography: 75, 92, 133, 179, 180, 212, 242, 274, 328, 451, 463, 550, 610, 705, 791, 897, 952, 991, 1009, 1086, 1105, 1170, 1362, 1367, 1380, 1384.

The energy emitted as LUMINESCENCE (fluorescence and/or phosphorescence) is derived from the energy absorbed from the incident light.

Most molecules have a SINGLET GROUND STATE (S_0) (Fig. 16.1). The only excited states which may be reached directly by light absorption are EXCITED SINGLET STATES ($S_1, S_2, S_3, \dots, S_n$). S_1 differs from S_0 in many

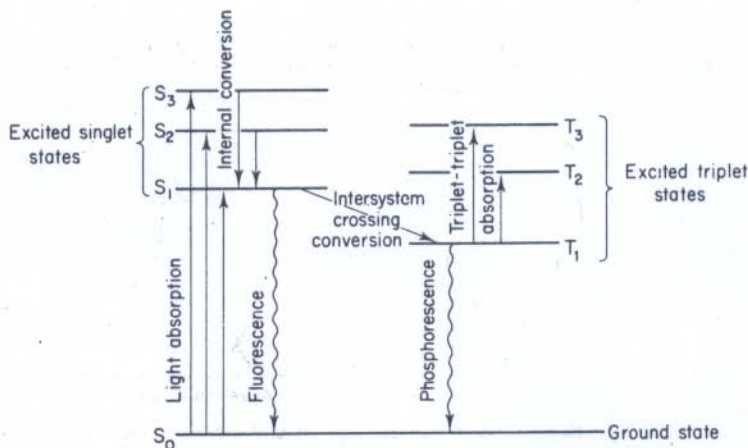


Fig. 16.1. Diagram showing the most important processes involving electronically excited states

ways and should be regarded as a chemically distinct species. The spins of electrons are paired in excited singlet states (S_1, \dots, S_n). The lifetime of an excited singlet state (S_1) is about 10^8 – 10^{10} s.

By the INTERSYSTEM CROSSING CONVERSION (a non-radiative process occurring with spin inversion) a molecule from excited singlet state (S_1) can reach the FIRST TRIPLET STATE (T_1). The lifetime of a triplet state (T_1) is from minutes to 10^{-3} s.

The HIGHER TRIPLET STATES (T_2, T_3, \dots, T_n) may be formed only when a molecule in its lowest triplet state (T_1) absorbs a new photon. Such a process is called TRIPLET-TRIPLET ABSORPTION.

An electronically excited molecule can lose its energy by emission of radiation which is known as luminescence. There are the following kinds of emission:

- (i) FLUORESCENCE is a radiative emission process occurring from the lowest excited singlet state (S_1) to the singlet ground state (S_0) (Fig. 16.1);
- (ii) PHOSPHORESCENCE is a radiative emission process occurring from the lowest excited triplet state (T_1) to the singlet ground state (S_0) (Fig. 16.1);
- (iii) EXCIMER FLUORESCENCE is a radiative emission process occurring as a result of the decomposition of the EXCIMER COMPLEX formed between the lowest excited singlet state (S_1) and the singlet ground state (S_0) (Fig. 16.1) (cf. Section 16.1);
- (iv) DELAYED FLUORESCENCE is a radiative emission process occurring from the decomposition of the EXCIMER COMPLEX formed between excited triplet states (T_1) (cf. Section 16.1).

Relations between absorption and emission spectra are shown in Fig. 16.2.

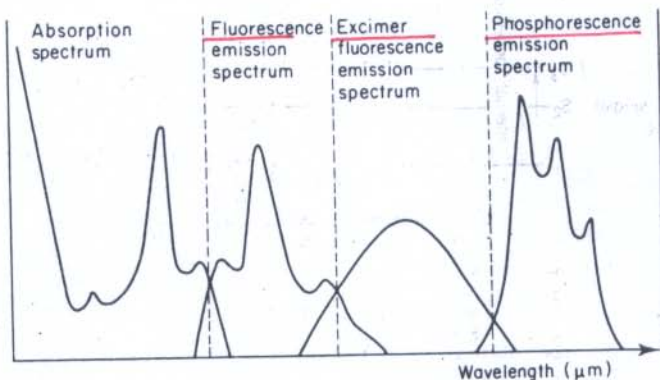


Fig. 16.2 Relations between absorption and emission spectra

An electronically excited molecule can also lose its energy by non-radiative processes such as the following:

- (i) INTERNAL CONVERSION is a non-radiative process between two different electronic states of the same multiplicity, i.e. $S_n \rightarrow S_1$, or $T_n \rightarrow T_1$. In this process an electronically excited molecule can lose its energy by conversion to heat.
- (ii) NON-RADIATIVE ENERGY TRANSFER is a process of transformation of energy from a singlet (or triplet) excited molecule (DONOR) to a molecule in the singlet ground state (ACCEPTOR).
- (iii) DISSOCIATION is a process whereby excitation energy is used to stimulate the decomposition of a molecule into free radicals.

The UNIMOLECULAR LIFETIME (τ) of an excited state is defined in general as the time in seconds required for the concentration of molecules in that state to decay to $1/e$ of its initial value; e is the base of natural logarithms.

The INHERENT RADIATIVE LIFETIME (τ_0) of an excited state is defined as the time in seconds required for the concentration of molecules in that state to decay to $1/e$ of its initial value if no radiationless processes occur.

(i) for fluorescence emission,

$$\Phi_f \tau_{0(f)} = \tau_f; \quad (16.1)$$

(ii) for phosphorescence emission,

$$\tau_p \left(\frac{1 - \Phi_f}{\Phi_p} \right) = \tau_{0(p)}; \quad (16.2)$$

where

τ is the unimolecular lifetime (measured time) (in seconds),

τ_0 is the inherent radiative lifetime (in seconds),

✓ Φ is the quantum yield of the emission process,

subscripts f and p mean fluorescence and phosphorescence, respectively.

✓ QUANTUM YIELD OF LUMINESCENCE is defined as the number of quanta emitted per exciting quantum absorbed.

The QUANTUM YIELD OF FLUORESCENCE (Φ_f) is defined as

$$\Phi_f = \frac{\text{Number of fluorescence quanta emitted}}{\text{Number of quanta absorbed to a singlet excited state}} \quad (16.3)$$

The QUANTUM YIELD OF PHOSPHORESCENCE (Φ_p) is defined as

$$\Phi_p = \frac{\text{Number of quanta phosphorescence emitted}}{\text{Number of quanta absorbed to a singlet excited state}} \quad (16.4)$$

The quantum yield is the most difficult characteristic to measure.

16.1 EXCIMERS AND EXCIPLEXES

An EXCIMER is a molecular dimer aggregate formed between an excited molecule in the lowest excited singlet state (S_1) and a molecule in the singlet ground state (S_0). Excimers are unstable in their ground state but are stable under electronic excitation:



During the decomposition of an EXCIMER COMPLEX one may observe EXCIMER FLUORESCENCE, which differs from 'normal' fluorescence:



Excimer fluorescence shows a broad characteristic spectrum without vibrational structure (Fig. 16.2) and is dependent on temperature.

Excimers may also result from reactions of two excited triplet states (T_1) (BIMOLECULAR TRIPLET-TRIPLET INTERACTION):



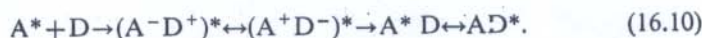
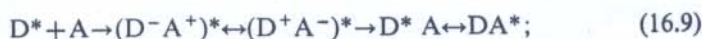
During the decomposition of such an excimer one may observe DELAYED FLUORESCENCE, which also differs from normal fluorescence:



DELAYED FLUORESCENCE is an emission which has the spectral properties of fluorescence but with a much longer rise and decay time than ordinary fluorescence. Frequently the decay time is of the same order of magnitude as the phosphorescence decay time. Delayed fluorescence depends upon the square of the incident light intensity because a triplet state (T_1) arises only from an initial excitation via an excited singlet state (S_1) and two such events are required to obtain fluorescence of this type. Delayed fluorescence is sensitive to oxygen, which quenches the triplet state (T_1) with great efficiency.

Excimers are formed in concentrated polymer solutions or in the solid state. In order for an excited molecule to form an excimer with another molecule, its counterpart should approach to within a distance of 3–4 Å from the excited molecule during the period of excitation. The probability of formation of an excimer is also dependent upon the spatial alignment of a pair of molecules and the parallel alignment for rigid planar aromatic rings in polymers.

An EXCIPLEX is a well-defined complex which exists only in electronically excited states. Exciplexes are formed between excited donor molecules (D^*) and acceptor molecules (A) or excited acceptor molecules (A^*) and donor molecules (D):



Charge-transfer
complex

The fluorescence emission from an exciplex is dependent on solvent polarity. With increasing solvent polarity there is a decrease in the fluorescence quantum yield.

Triplet exciplexes can be identified in several cases by measuring phosphorescence and by triplet-triplet absorption.

Bibliography: 138, 464, 465, 528, 974, 1242.

References: 2041, 2414, 3019, 3035, 3066–3069, 3451, 3465, 3466, 3479, 3630, 3910, 4065, 4142, 4244–4246, 4611, 4612, 5095, 5195, 5507, 5835, 6015, 6016, 6482, 6753–6756, 6905, 7002, 7240, 7271.

16.2 FLUORESCENCE

FLUORESCENCE is a radiative emission process occurring from the lowest excited singlet state (S_1) to the singlet ground state (S_0) (Fig. 16.1).

Electronic Interband Transitions

It came as a surprise that optical spectroscopy developed as an important experimental tool for the determination of band structure. First, the absorption and reflection bands of crystals are broad and apparently featureless functions of the photon energy when this is greater than the band gap. Second, direct interband absorption of a photon $\hbar\omega$ will occur at all points in the Brillouin zone for which energy is conserved:

$$\hbar\omega = \epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}), \quad (21)$$

where c is an empty band and v is a filled band. The total absorption at given ω is an integral over all transitions in the zone that satisfy (21).

Three factors unraveled the spectra:

- The broad bands are not like a spectral line greatly broadened by damping, but the bands convey much intelligence which emerges when derivatives are taken of the reflectance (Fig. 3); derivatives with respect to wavelength, electric field, temperature, pressure, or uniaxial stress, for example. The spectroscopy of derivatives is called modulation spectroscopy.
- The relation (21) does not exclude spectral structure in a crystal, because transitions accumulate at frequencies for which the bands c , v are parallel—that is, at frequencies where

$$\nabla_{\mathbf{k}}[\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})] = 0. \quad (22)$$

At these critical points in \mathbf{k} space the joint density of states $D_c(\epsilon_v + \hbar\omega)D_v(\epsilon_v)$ is singular, according to the same argument we used in (5.37) to show that the density of phonon modes $D(\omega)$ is singular when $\nabla_{\mathbf{k}}\omega$ is zero.

- The pseudopotential method for calculating energy bands helps identify the positions in the Brillouin zone of the critical points found in modulation spectra. Band-band energy differences can be calculated with an accuracy as good as 0.1 eV. The experimental results can then be fed back to give improvements in the pseudopotential calculations.

EXCITONS

Reflectance and absorption spectra often show structure for photon energies just below the energy gap, where we might expect the crystal to be transparent. This structure is caused by the absorption of a photon with the creation of a bound electron-hole pair. An electron and a hole may be bound together by their attractive coulomb interaction, just as an electron is bound to a proton to form a neutral hydrogen atom.

The bound electron-hole pair is called an exciton, Fig. 4. An exciton can move through the crystal and transport energy; it does not transport charge

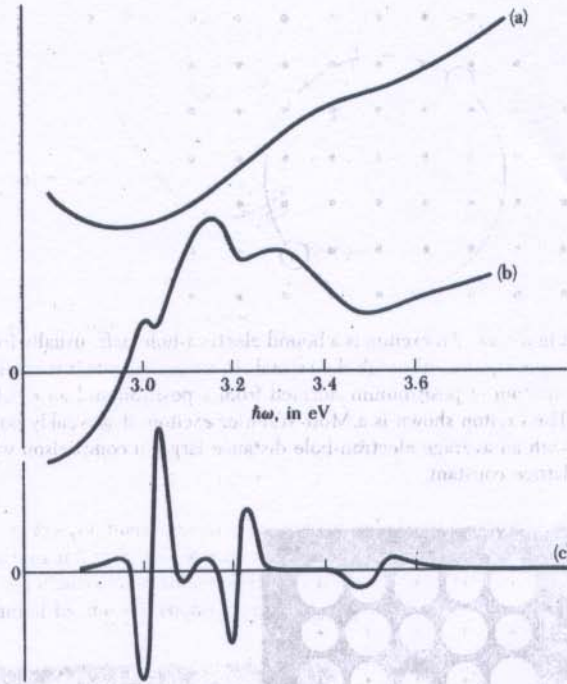


Figure 3 Comparison of (a) reflectance, (b) wavelength derivative reflectance (first derivative), and (c) electroreflectance (third derivative), of the spectral region in germanium between 3.0 and 3.6 eV. (After data by D. D. Sell, E. O. Kane, and D. E. Aspnes.)

because it is electrically neutral. It is similar to positronium, which is formed from an electron and a positron.

Excitons can be formed in every insulating crystal. When the band gap is indirect, excitons near the direct gap may be unstable with respect to decay into a free electron and free hole. All excitons are unstable with respect to the ultimate recombination process in which the electron drops into the hole. Excitons can also form complexes, such as a biexciton from two excitons.

We have seen that a free electron and free hole are created whenever a photon of energy greater than the energy gap is absorbed in a crystal. The threshold for this process is $\hbar\omega > E_g$ in a direct process. In the indirect phonon-assisted process of Chapter 8 the threshold is lower by the phonon energy $\hbar\Omega$. But in the formation of excitons the energy is lowered with respect to these thresholds by the binding energy of the exciton, which may be in the range 1 meV to 1 eV, as in Table 1.

Excitons can be formed by photon absorption at any critical point (22), for if $\nabla_{\mathbf{k}}\epsilon_v = \nabla_{\mathbf{k}}\epsilon_c$ the group velocities of electron and hole are equal and the particles may be bound by their coulomb attraction. Transitions leading to the formation of excitons below the energy gap are indicated in Figs. 5 and 6.

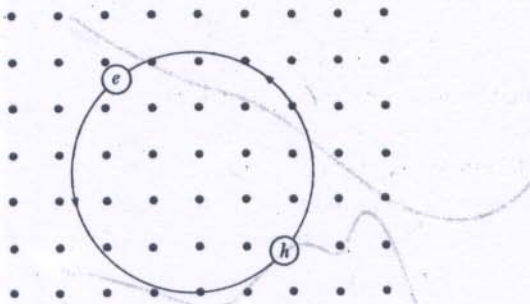


Figure 4a An exciton is a bound electron-hole pair, usually free to move together through the crystal. In some respects it is similar to an atom of positronium, formed from a positron and an electron. The exciton shown is a Mott-Wannier exciton: it is weakly bound, with an average electron-hole distance large in comparison with a lattice constant.

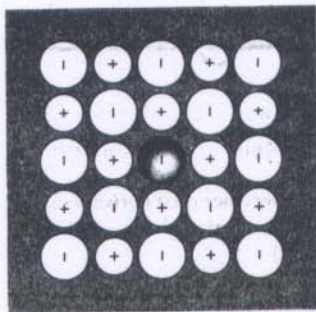


Figure 4b A tightly bound or Frenkel exciton shown localized on one atom in an alkali halide crystal. An ideal Frenkel exciton will travel as a wave throughout the crystal, but the electron is always close to the hole.

Table 1 Binding energy of excitons, in meV.

Si	14.7	BaO	56.	RbCl	440.
Ge	4.15	InP	4.0	LiF	(1000)
GaAs	4.2	InSb	(0.4)	AgBr	20.
GaP	3.5	KI	480.	AgCl	30.
CdS	29.	KCl	400.	TlCl	11.
CdSe	15.	KBr	400.	TlBr	6.

Data assembled by Frederick C. Brown and Arnold Schmidt.

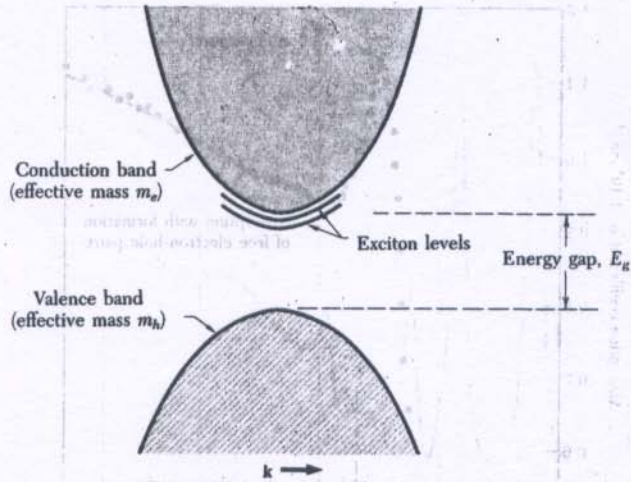


Figure 5 Exciton levels in relation to the conduction band edge, for a simple band structure with both conduction and valence band edges at $k = 0$. An exciton can have translational kinetic energy. Excitons are unstable with respect to radiative recombination in which the electron drops into the hole in the valence band, accompanied by the emission of a photon or phonons.

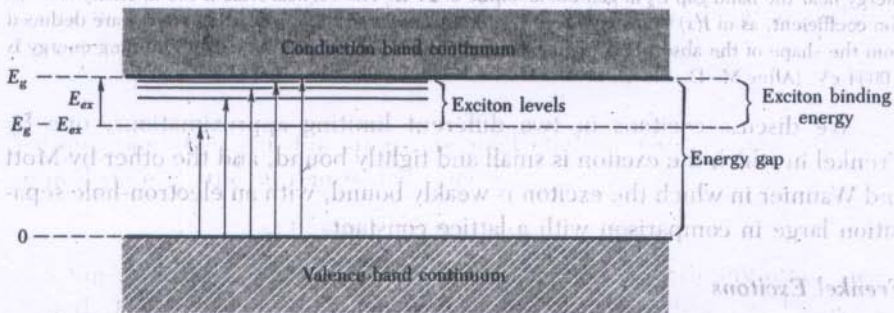


Figure 6 Energy levels of an exciton created in a direct process. Optical transitions from the top of the valence band are shown by the arrows; the longest arrow corresponds to the energy gap. The binding energy of the exciton is E_{ex} , referred to a free electron and free hole. The lowest frequency absorption line of the crystal at absolute zero is not E_{ex} , but is $E_g - E_{ex}$.

The binding energy of the exciton can be measured in three ways:

- In optical transitions from the valence band, by the difference between the energy required to create an exciton and the energy to create a free electron and free hole, Fig. 7.
- In recombination luminescence, by comparison of the energy of the free electron-hole recombination line with the energy of the exciton recombination line.
- By photo-ionization of excitons, to form free carriers. This experiment requires a high concentration of excitons.

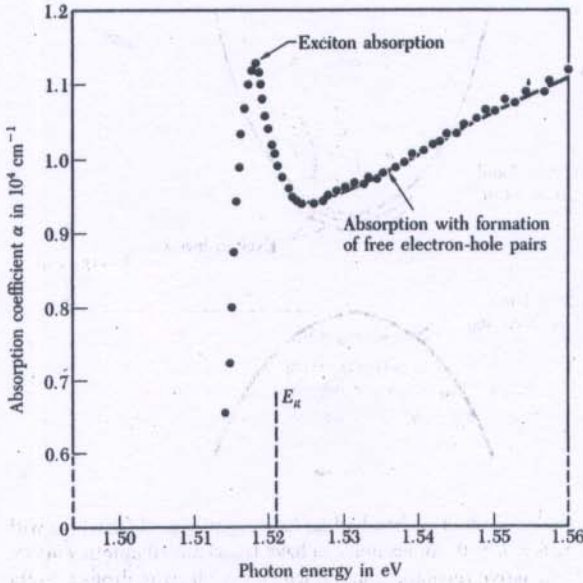


Figure 7 Effect of an exciton level on the optical absorption of a semiconductor for photons of energy near the band gap E_g in gallium arsenide at 21 K. The vertical scale is the intensity absorption coefficient, as in $I(x) = I_0 \exp(-\alpha x)$. The energy gap and exciton binding energy are deduced from the shape of the absorption curve: the gap E_g is 1.521 eV and the exciton binding energy is 0.0034 eV. (After M. D. Sturge.)

We discuss excitons in two different limiting approximations, one by Frenkel in which the exciton is small and tightly bound, and the other by Mott and Wannier in which the exciton is weakly bound, with an electron-hole separation large in comparison with a lattice constant.

Frenkel Excitons

In a tightly bound exciton (Fig. 4b) the excitation is localized on or near a single atom: the hole is usually on the same atom as the electron although the pair may be anywhere in the crystal. A Frenkel exciton is essentially an excited state of a single atom, but the excitation can hop from one atom to another by virtue of the coupling between neighbors. The excitation wave travels through the crystal much as the reversed spin of a magnon travels through the crystal.

The crystalline inert gases have excitons which in their ground states correspond to the Frenkel model. Atomic krypton has its lowest strong atomic transition at 9.99 eV. The corresponding transition in the crystal is closely equal and is at 10.17 eV, Fig. 8. The energy gap in the crystal is 11.7 eV, so the exciton ground state energy is $11.7 - 10.17 = 1.5$ eV, referred to a free electron and free hole separated and at rest in the crystal.

The translational states of Frenkel excitons have the form of propagating waves, like all other excitations in a periodic structure. Consider a crystal of N