TRANSITION PROBABILITIES, ABSORPTION COEFFICIENTS AND OSCILLATOR STRENGTHS IN CS_2

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A "system," e.g., an atom or molecule, is in a space containing radiation of density $\rho(\nu)$. If it is initially in a state "1" and if state "2" can exist, with $E_2 > E_1$, it will eventually absorb a photon of frequency $(E_2 - E_1)/h$ and be excited to state 2. The probability per unit time that this event will occur is $B\rho(\nu)$. Here B is the "Einstein probability for absorption," and $\rho(\nu)$ is energy per unit volume per unit frequency range. That is,

$\rho(\nu)d\nu$ = energy per unit volume in the frequency range $d\nu$.

= $h\nu$ times number of photons per unit volume with frequency in $(\nu, \nu + d\nu)$.

$B\rho(\nu)$ has dimension 1/sec.

The formula for B in cgs (esu) units is:

$$B = \frac{8\pi^3}{3h^2} |M_{12}| \tag{1}$$

Where M_{12} is the "dipole moment" of the system:

$$(M_x)_{12} = \int u_2^* \Sigma e_j x_j u_1 dv \tag{2}$$

with similar expressions for M_y and M_z. Then

$$|M_{12}|^2 = (M_x)_{12}^2 + (M_y)_{12}^2 + (M_z)_{12}^2$$

and e_j is the charge on the jth particle of the system, located at $\vec{r}_j$. $|M_{12}|^2$ has dimensions charge^2 x length^2 = erg cm^3.

If the system under inspection is exposed to a beam of radiation with energy flux $I(\nu)$, the mean density of radiation surrounding the particle is $\rho(\nu) = I(\nu)/c$ and the transition probability per second is

$$B\rho(\nu) = BI(\nu)/c \tag{3}$$

with each transition, the particle absorbs a photon of energy $h\nu_{12}$. So, the energy absorbed per second is

$$\Delta W = Bh\nu I(\nu)/c \tag{4}$$

Consider an ensemble of N such systems contained in unit volume and bathed uniformly in monochromatic radiation of frequency ν. When ν is far removed from the resonant frequency ν_{12}, energy absorbed from the beam will be very small. As ν is swept through resonance, the rate of energy absorption rises to a maximum and falls again to near zero for $\nu >> \nu_{12}$. It is implicit in the conditions for which Eq. (1) is derived that $\rho(\nu)$ should be continuous in the neighborhood of the resonance and that the transition probability given by Eq. (3) should include transitions due to off-resonance absorptions as well as resonance absorptions. If we define an absorption cross section $\sigma(\nu)$, then the total energy absorbed per sec and per cm^3 is

$$N\Delta W = N\int\sigma(\nu)I(\nu)d\nu \tag{5}$$

where $I(\nu)d\nu$ = energy flowing through unit area in unit time in the frequency interval $(\nu, \nu + d\nu)$, and N is the number of systems per unit volume.

If we keep in mind that $I(\nu)$ is essentially constant over the absorption curve we find that

$$I(\nu_{12})\int_{\nu_{12}-\varepsilon}^{\nu_{12}+\varepsilon} \sigma(\nu)d\nu = I(\nu_{12})\,\frac{Bh\nu}{c} \tag{6}$$

so that

$$\frac{Bh\nu}{c} = \int \sigma(\nu)d\nu \tag{7}$$

For a beam with energy flux $I(\nu)d\nu$, the energy per second removed from the beam by a layer of thickness dx normal to the beam is

$$d[I(\nu,x)d\nu] = I(\nu,x)d\nu \cdot N \cdot \sigma dx \tag{8}$$

or

$$I(\nu,x) = I(\nu,o)e^{-N\sigma x} \tag{9}$$

where N is the number of systems per unit volume, as before. Since σ is a function of ν, it's clear that a beam of broad-band radiation incident on such a layer will have its spectral distribution changed by passage through the layer. If $\sigma(\nu)$ has the form shown in Fig. 1a, a uniform spectrum will be altered to the form shown in Fig. 1b.

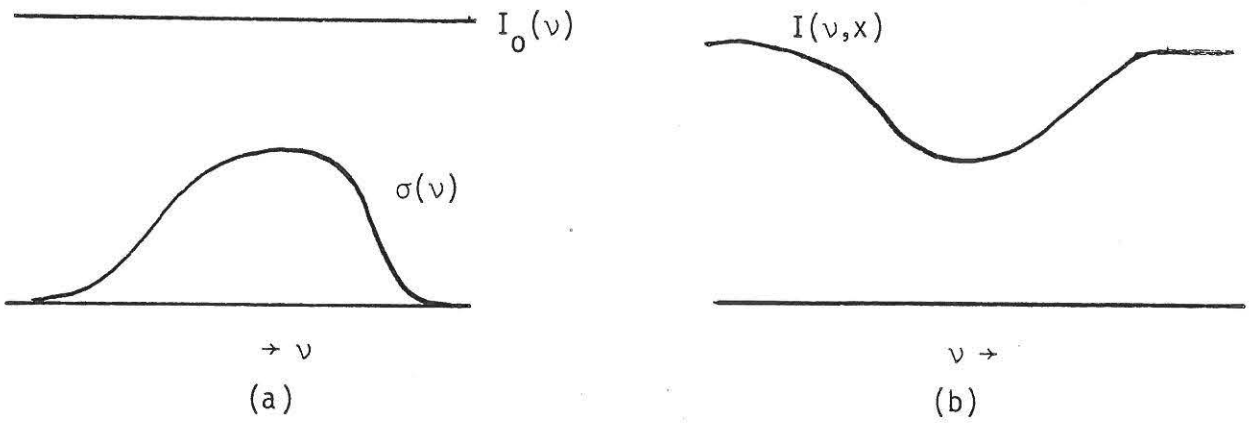

Fig. 1

Effect of an absorption band on a uniform spectrum. (a) Absorption cross section and initial spectral distribution of intensity. (b) Intensity distribution after passing through a layer of thickness x.

Eq. (8) can be integrated over frequency to yield the equation

$$\int_{\nu_1}^{\nu_2} \frac{dI(\nu,x)}{dx}\, d\nu \;=\; -N\int_{\nu_1}^{\nu_2} I(\nu,x)\sigma(\nu)d\nu \tag{10}$$

or

$$\frac{d}{dx}\int_{\nu_1}^{\nu_2} I(\nu,x)d\nu \;=\; -N\,\overline{\sigma}\int_{\nu_1}^{\nu_2} I(\nu,x)d\nu \tag{11}$$

The theorem of the mean for integrals has been used in Eq. (11) and

$$\overline{\sigma} \;\equiv\; \sigma(\nu_m) \;\equiv\; \overline{\sigma}(x)$$

where ν_m is a number lying between ν_1 and ν_2 which may, and usually will, vary with x. With

$$F(x) \;\equiv\; \int_{\nu_1}^{\nu_2} I(\nu,x)dx$$

Eq. (11) can be integrated to yield

$$F(x) \;=\; F(0)\,\exp\Big[-N\int_0^x \overline{\sigma}\,(x)dx\Big]$$

$$\;=\; F(0)\,\exp(-N\overline{\overline{\sigma}}x) \tag{12}$$

The significance of Eq. (12) is that there exists a number $\bar{\bar{\sigma}}$ for each x such that Eq. (11) expresses the relation between $F(x)$ and $F(o)$. If measurement shows that $\bar{\bar{\sigma}}$ varies but little over a significant range of x, it is at least a useful mnemonic.

An alternative procedure is to write Eq. (10) as

$$\frac{d}{dx}\int_{\nu_1}^{\nu_2} I(\nu,x)d\nu = -N\bar{I}(x)\int_{\nu_1}^{\nu_2}\sigma(\nu)d\nu \qquad (13)$$

This equation is useful if $N\sigma x << 1$ and $I(\nu,o)$ is constant in (ν_1,ν_2). Then

$$\int_{\nu_1}^{\nu_2} I(\nu,x)d\nu \equiv \bar{I}(x)(\nu_2 - \nu_1)$$

and

$$\frac{d}{dx}\int_{\nu_1}^{\nu_2} I(\nu,x)d\nu = \frac{d\bar{I}(x)}{dx}(\nu_2 - \nu_1) = -N\bar{I}(x)\int_{\nu_1}^{\nu_2}\sigma(\nu)d\nu$$

or

$$\Delta\bar{I}(x) = -\bar{I}(x)\,N\frac{\int_{\nu_1}^{\nu_2}\sigma(\nu)d\nu}{(\nu_2 - \nu_1)}\Delta x \qquad (14)$$

This is a useful experimental relation, but must be applied only when $\Delta\bar{I}/\bar{I} << 1$.

If we define

$$\bar{\sigma} \equiv \int_{\nu_1}^{\nu_2} \sigma(\nu)d\nu/(\nu_2 - \nu_1)$$

Eq. (14) becomes

$$\Delta\bar{I}(x) = -\bar{I}(x)\, N\, \bar{\sigma}\Delta x \qquad (15)$$

$N\bar{\sigma}$ is sometimes called the absorption coefficient of the materials in the region (ν_1, ν_2).

Comparison of Eqs. (7) and (15) shows that

$$\bar{\sigma} = (Bh\nu/c)/(\nu_2 - \nu_1) \qquad (16)$$

which has dimensions cm^2.

As an example of the application of these relations, consider shot 81-014. Cell thickness was between 0.5 and 1.0 micron, say 0.75. $\Delta\bar{I}/\bar{I} \simeq -0.5$, which violates the conditions under which Eq. (15) is valid. But, for the present purpose it will serve. Then,

$$\Delta x = 0.75 \times 10^{-4} \text{ cm}$$

$$\Delta\bar{I}/\bar{I} = -0.5$$

$$N = A\rho/76.13 = 6.022 \times 10^{23} \times 1.261/76.13$$

$$= 9.97 \times 10^{21}/\text{cc}$$

$$\bar{\sigma} = \frac{-\Delta\bar{I}/\bar{I}}{N\Delta x} = 6.68 \times 10^{-19} \text{ cm}^2$$

The center frequency for the band is 31066 cm^{-1}, the upper band edge is 33602 cm^{-1}, the lower edge is 29386 cm^{-1}. These numbers substituted into Eq. (16) give

$$B = \frac{C\bar{\sigma}}{h}\frac{\nu_2 - \nu_1}{\nu} = 4.12 \times 10^{17} \text{ cm/g}$$

Oscillator strength is

$$f = \frac{Meh\nu}{\pi e^2} B$$

$$= 7.753 \times 10^{-21} B$$

$$= \underline{3.2 \times 10^{-3}}$$

For comparison, Penner* gives the following values for f in other materials (p. 28)

Molecule	Transition	Wave Number	f
OH	$^2\Pi \rightarrow {}^2\Sigma$	32,600 cm^{-1}	1.2×10^{-3}
CN	$^2\Sigma \rightarrow {}^2\Pi$	9,117	2.0×10^{-2}
C_2	$^1\Sigma_g^+ \rightarrow {}^1\Pi u$	8,268	2.0×10^{-2}

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* S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley, 1959.

The square of the transition element is

$$|M|^2 = \frac{3h^2}{8\pi^3} B = 5.308 \times 10^{-55} B = 2.187 \times 10^{-37} \text{ erg cm}^3$$

and

$$\frac{|M|^2}{e^2} = |x|^2 = 9.48 \times 10^{-19} \text{ cm}^2$$

This compares with the value given by Heitler† for a classical oscillator (p. 108):

$$|x_c|^2 = 5.79 \times 10^{-11} \lambda = 1.865 \times 10^{-15}.$$

The relative small value of f or $|x|^2/|x_c|^2$ reflects the nature of the transition, which may be a forbidden singlet to triplet transition and which depends upon bending of the molecule.

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† W. Heitler, Quantum Theory of Radiation, 2nd Edition.