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Quantities and Units in Spectroscopy

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1.1. Introduction

The accurate definition of quantities and the units to be used for their numerical values is always a critical topic in science, especially in physics and chemistry. In the domain of atomic and molecular sciences, the International Union of Pure and Applied Chemistry (IUPAC) has worked on detailed and strict recommendations for this, which can be found in the so-called “Green Book” (Cohen et al. 2007). This book presents which symbol and typography should be used in each case, as well as the recommended units to be used that are mostly SI units.

Nevertheless, many specific domains have their own traditions and are often strongly attached to them. This is reflected in this series of books about high-resolution molecular spectroscopy, for which we did not ask the various authors to change their texts in order to fully comply with IUPAC’s recommendations. Thus, this first chapter is dedicated to the definition of several general quantities, along with some comments about common usages and units. What is presented here is relevant for the *Theory*, *Experiment* and *Applications* volumes, but is restricted to common

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general quantities. Other very specific quantities used for restricted domains will be defined in each chapter. Readers can also refer to Loëte (1984); Šimečková et al. (2006); Rao and Weber (1992) for further detail.

1.2. Energy and associated quantities

Absorption, emission or scattering spectra are represented by a curve of light intensity (whatever this term means, see section 1.3) as a function of a quantity related to the energy of the incident or exciting light. This quantity and the unit used depends on the spectral domain, since each of them is studied through different techniques and conforming to different uses and traditions.

The first possibility is to use the *wavelength*, with symbol λ . This represents the spatial distance between successive crests of an electromagnetic wave. Dispersive optical elements (prisms, diffraction gratings, etc.) allow us to build spectrometers that directly give data as a function of λ (the dispersion angle depending directly on it). Thus, low-resolution spectra are often provided as functions of wavelength. We should note that this is always the wavelength in vacuum that is considered. The wavelength unit used simply depends on the spectral domain, from Ångströms or nanometers at high energies (γ , X and UV rays) to micrometers in the visible and infrared ranges. Radiowave studies even use bigger meter multiples such as centimeters or kilometers.

The *wavenumber*, with symbol $\tilde{\nu}$, is extensively used in the infrared and visible ranges. This is the inverse of the wavelength, that is:

$$\tilde{\nu} = \frac{1}{\lambda} \quad [1.1]$$

The symbol σ is also sometimes used, although IUPAC (Cohen et al. 2007) recommends to use it only in a medium and not in vacuum. The traditional unit is cm^{-1} .

The *frequency*, with symbol ν , represents the time interval between successive crests of an electromagnetic wave. We have the relations:

$$\nu = \frac{c}{\lambda} = \frac{c}{\tilde{\nu}}, \quad [1.2]$$

with c being the speed of light in vacuum ($299\,792\,458\,\text{m s}^{-1}$). It is especially used in the microwave in terahertz domains. The units used are multiples of the hertz (Hz) (or s^{-1}) like kHz, MHz, GHz and THz.

We can also encounter the *angular frequency*, with symbol ω , which is:

$$\omega = 2\pi\nu \quad [1.3]$$

and whose unit is rad s^{-1} . This mostly appears in theoretical descriptions of molecular vibrations.

The *energy* E is itself the fundamental quantity, which is exchanged between matter and photons. We have the relations:

$$E = \hbar\omega = h\nu = \frac{c}{\lambda} = \frac{c}{\tilde{\nu}}, \quad [1.4]$$

where h is Planck's constant ($6.626\,070\,15 \times 10^{-34} \text{ J s}$) and $\hbar = h/2\pi$.

Spectra may be represented as functions of energy in very short wavelength domains, like ultraviolet X or γ . Although the SI unit for energy is the Joule, the values we can encounter in spectroscopy are usually very small, and other traditional units are in use, especially electron-volts (with $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). Quite rarely, we can still encounter the erg, an old non-SI unit ($1 \text{ erg} = 1 \times 10^{-7} \text{ J}$).

1.3. Intensity

The question of “intensity” in spectroscopy is quite difficult, since this terms covers several notions and is used by various authors in different ways. We try here to provide a short (and maybe not exhaustive) summary of this topic, with the most common definitions.

Light *intensity* $I(\tilde{\nu})$ absorbed at wavenumber $\tilde{\nu}$ (in cm^{-1}) per surface unit by a gas layer with thickness L at pressure P is expressed through the Beer–Lambert law:

$$I(\tilde{\nu}) = I_0(\tilde{\nu})e^{-k(\tilde{\nu}, P)L}, \quad [1.5]$$

where:

– $I_0(\tilde{\nu})$ is the intensity of incident light (power per surface unit, typically expressed in W cm^{-2}).

– $k(\tilde{\nu}, P)$ is the *absorption coefficient*:

$$k(\tilde{\nu}, P) = \frac{1}{L} \log \frac{I_0(\tilde{\nu})}{I(\tilde{\nu})} = \frac{1}{L} A(\tilde{\nu}), \quad [1.6]$$

with $A(\tilde{\nu})$ being the unitless *absorbance*. If L is expressed in cm, then $k(\tilde{\nu}, P)$ is expressed in cm^{-1} .

In particular, at the center of a given spectral line corresponding to a transition between energy levels i and f , say $\tilde{\nu}_{if}$ (in cm^{-1}), we can consider the height of the line per unit length of the absorbing medium, or *opacity* at $\tilde{\nu}_{if}$, $k(\tilde{\nu}_{if}, P)$, which is expressed in cm^{-1} .

The *line strength* or *integrated absorption coefficient* for a transition centered around $\tilde{\nu}_{if}$ between an initial state i and a final state f is:

$$S_{if}(P) = \int_0^\infty k(\tilde{\nu}, P) d\tilde{\nu}. \quad [1.7]$$

It depends on the pressure and is expressed in cm^{-2} . This represents the line area in the absorbance spectrum.

It is usual to use the *line strength per pressure unit*:

$$S_{if}^P = \frac{S_{if}(P)}{P}, \quad [1.8]$$

which is expressed in $\text{cm}^{-2} \text{atm}^{-1}$ (P being expressed in atmospheres). We thus have:

$$S_{if}^P P L = \int_0^\infty \log \frac{I_0(\tilde{\nu})}{I(\tilde{\nu})} d\tilde{\nu} = \int_0^\infty A(\tilde{\nu}) d\tilde{\nu}. \quad [1.9]$$

Another quantity, which is for instance used in the HITRAN database, is the *integrated line cross-section* that is the integrated absorption coefficient per molecule per unit volume at a given pressure P , that is:

$$S_{if}^N = \frac{S_{if}(P)}{N}, \quad [1.10]$$

where N , expressed in molecule cm^{-3} , is the number of molecules per unit volume. For an ideal gas at temperature T and pressure P , it is:

$$N = L \frac{T_0}{T} \frac{P}{P_0}, \quad [1.11]$$

$L = 2.686\,777\,4 \times 10^{19}$ molecule cm^{-3} being the Loschmidt number¹, $T_0 = 273.15$ K and $P_0 = 1$ atm. The unit of S_{if}^N is thus $\text{cm}^{-1} / (\text{molecule cm}^{-2})$ (the so-called “HITRAN unit”) and we have:

$$S_{if}^P(\text{cm}^{-2} \text{ atm}^{-1}) = \frac{L}{P_0} \frac{T_0}{T} S_{if}^N(\text{cm}^{-1} / (\text{molecule cm}^{-2})). \quad [1.12]$$

In the HITRAN database, S_{if}^N is defined at $T = 296$ K.

For a system in thermodynamic equilibrium that obeys the Maxwell–Boltzmann statistics, we can relate the line strength to *Einstein’s induced absorption coefficient* $B_{i \rightarrow f}$ (Šimečková et al. 2006) through:

$$S_{if}^N = \frac{h}{cQ} \tilde{\nu}_{if} g_i \left(e^{-\frac{E_i}{k_B T}} - e^{-\frac{E_f}{k_B T}} \right) B_{i \rightarrow f}, \quad [1.13]$$

where $h = 6.626\,069\,57 \times 10^{-34}$ J s is Planck’s constant, $k_B = 1.380\,648\,8 \times 10^{-23}$ J K⁻¹ is Boltzmann’s constant, $c = 29\,979\,245\,800$ cm s⁻¹ is the speed of light in vacuum, Q is the dimensionless partition function, E_i is the energy of the initial state in Joules and g_i is the dimensionless statistical weight of initial state i . S_{if}^N is thus proportional to the population difference between the initial and final states. If E_f is the energy of the final state in Joules, we can note that:

$$\tilde{\nu}_{if} = \frac{E_f - E_i}{hc}, \quad [1.14]$$

which leads to the following form of the previous equation, which is generally used for absorption spectra (the term in parentheses being in general close to 1):

$$S_{if}^N = \frac{h}{cQ} \tilde{\nu}_{if} g_i e^{-\frac{E_i}{k_B T}} \left(1 - e^{-\frac{hc\tilde{\nu}_{if}}{k_B T}} \right) B_{i \rightarrow f}. \quad [1.15]$$

Einstein’s stimulated emission coefficient $B_{f \rightarrow i}$ is related to $B_{i \rightarrow f}$ through:

$$B_{f \rightarrow i} = \frac{g_i}{g_f} B_{i \rightarrow f}, \quad [1.16]$$

¹ $L = \frac{1}{k_B} \frac{P_0}{T_0}$ where k_B is Boltzmann’s constant. If $\mathcal{N}$ is the number of molecules, V is the volume at P and T , N_A is the Avogadro number and $n = \frac{\mathcal{N}}{N_A}$ is the number of moles, then $N = \frac{\mathcal{N}}{V} = \frac{1}{k_B} \frac{P}{T}$, that is, $PV = \mathcal{N}k_B T = \frac{\mathcal{N}}{N_A} RT = nRT$, which is the ideal gas law, since the ideal gas constant R is $R = k_B N_A$.

where g_f is the dimensionless statistical weight of final state f . $B_{i \rightarrow f}$ and $B_{f \rightarrow i}$ are expressed in $\text{cm}^3(\text{J s}^2)^{-1}$.

Finally, *Einstein's spontaneous emission coefficient* $A_{f \rightarrow i}$ is:

$$A_{f \rightarrow i} = 8\pi h \tilde{\nu}_{if}^3 B_{f \rightarrow i} \quad [1.17]$$

and it is expressed in s^{-1} .

It can be shown that $B_{i \rightarrow f}$ is related to the matrix elements of the dipole moment components μ_A ($A = X, Y$ or Z being the laboratory fixed axes) through:

$$B_{i \rightarrow f} = \frac{8\pi^3}{3h^2 g_i} \sum_{A=X,Y,Z} \sum_{\alpha_i, \alpha_f} |\langle i, \alpha_i | \mu_A | f, \alpha_f \rangle|^2, \quad [1.18]$$

where α_i and α_f represent all intermediate quantum numbers for the initial and final states, respectively. In an isotropic gas medium, all components μ_A have the same matrix elements and we have the formula (the one used in the formalism (Boudon et al. 2011) and programs (Wenger et al. 2008) of the Dijon group):

$$S_{if}^P(\text{cm}^{-2} \text{atm}^{-1}) = \frac{8\pi^3}{hcQ} L \frac{T_0}{T} \tilde{\nu}_{ij} e^{-\frac{E_i}{k_B T}} \left(1 - e^{-\frac{hc\tilde{\nu}_{if}}{k_B T}} \right) \quad [1.19]$$

$$\times \sum_{\alpha_i, \alpha_f} |\langle i, \alpha_i | \mu_Z | f, \alpha_f \rangle|^2, \quad [1.20]$$

where we have assumed $P_0 = 1 \text{ atm}$.

Table 1.1 summarizes all these quantities and their units. Figure 1.1 explains these quantities schematically. See also Rao and Weber (1992) for conversion relations between these quantities. We can simply mention that the *line strength per pressure unit* (in $\text{cm}^{-2} \text{atm}^{-1}$) at temperature T can be converted to the *integrated line cross-section* in $\text{cm}^{-1} / (\text{molecule cm}^{-2})$, the so-called “HITRAN unit” (Gordon et al. 2022), by dividing by $7.338933 \times 10^{21}/T$.

Finally, it should be mentioned that, in some specific cases, absolute intensity values cannot be measured, and only relative intensities are accessible. Those are thus given using *arbitrary units*. This is, for instance, the case for Raman scattering spectra.

Name	Symbol	Typical unit
Intensity	I	W cm^{-2}
Absorbance	A	unitless
Absorption coefficient or opacity	k	cm^{-1}
Line strength	S_{if}	cm^{-2}
Line strength per pressure unit	S_{if}^P	$\text{cm}^{-2} \text{atm}^{-1}$
Integrated line cross-section	S_{if}^N	$\text{cm}^{-1} / (\text{molecule cm}^{-2})$
Einstein's induced absorption coefficient	$B_{i \rightarrow f}$	$\text{cm}^3 (\text{J s}^2)^{-1}$
Einstein's stimulated emission coefficient	$B_{f \rightarrow i}$	$\text{cm}^3 (\text{J s}^2)^{-1}$
Einstein's spontaneous emission coefficient	$A_{f \rightarrow i}$	s^{-1}

Table 1.1. Summary of intensity-related quantities and units

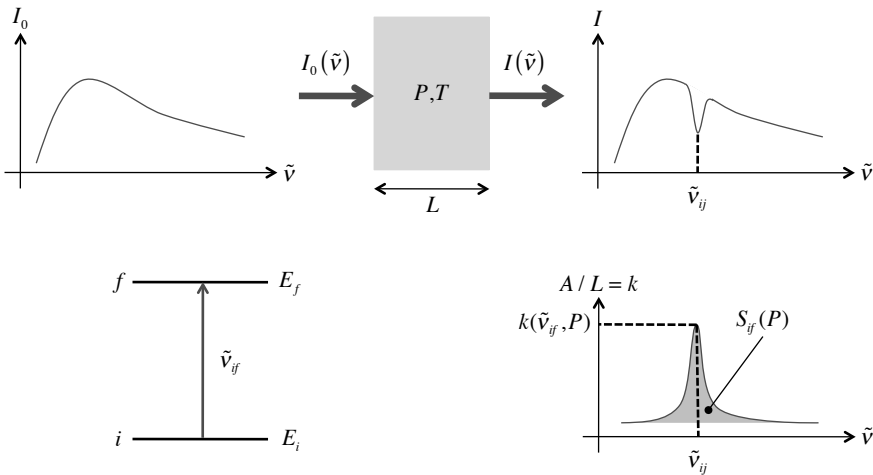


Figure 1.1. The absorption process and the definition of opacity k ; line strength S_{if}

1.4. Line shape quantities

As for the question of spectral lineshapes, the situation is simpler, at least in a basic approach. We can define three basic quantities in the main general case, these ones being used for instance in the HITRAN database. Further details can be found in the “Isolated line shape” chapter of the present series of books. Some other specific elements, such as line-mixing parameters, are also presented directly in the corresponding chapters.

The *line broadening coefficient* with symbol γ , which may originate either from collisions within the considered gas itself (self-broadening) or from collisions with a foreign gas (air, O₂, N₂, etc.), is measured in cm⁻¹ atm⁻¹.

The *pressure line shift* with symbol δ , which may also originate either from collisions within the considered gas itself (self shift) or from collisions with a foreign gas (air, O₂, N₂, etc.), is measured in cm⁻¹ atm⁻¹.

The *temperature exponent* for line broadening coefficients, with symbol n , is unitless. At a given temperature T , we have:

$$\gamma(T) = \gamma(T_0) \left(\frac{T_0}{T} \right)^n, \quad [1.21]$$

where $T_0 = 296$ K.

1.5. Other quantities

Let us finally define some other quantities related to molecular concentrations and light flux.

The *column density* N is the number of molecules per unit area integrated over the optical path, and is measured in molecule cm⁻².

The *concentration* or *number density* n counts the number of molecules per unit volume. It can be either an absolute value in molecule cm⁻³, a relative value in mass in ppm, ppb, ppt, etc., or a relative value in volume in ppmv, ppbv, pptv, etc.

The *spectral flux density* or *spectral flux irradiance* is the signal power per surface unit per frequency unit. Traditionally, astrophysicists measure it in Janskys (Jy), where 1 Jy = 10⁻²⁶ W m⁻² Hz⁻¹.

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