

7.1: Introduction

Atomic spectroscopy is, of course, a vast subject, and there is no intention in this brief chapter of attempting to cover such a huge field with any degree of completeness, and it is not intended to serve as a formal course in spectroscopy. For such a task a thousand pages would make a good start. The aim, rather, is to summarize some of the words and ideas sufficiently for the occasional needs of the student of stellar atmospheres. For that reason this short chapter has a mere 26 sections.

Wavelengths of spectrum lines in the visible region of the spectrum were traditionally expressed in angstrom units (\AA) after the nineteenth century Swedish spectroscopist Anders Ångström, one \AA being 10^{-10}m . Today, it is recommended to use nanometres (nm) for visible light or micrometres (μm) for infrared. $1\text{ nm} = 10\text{ \AA} = 10^{-3}\mu\text{m} = 10^{-9}\text{m}$. The older word *micron* is synonymous with micrometre, and should be avoided, as should the isolated abbreviation μ . The usual symbol for wavelength is λ .

Wavenumber is the reciprocal of wavelength; that is, it is the number of waves per metre. The usual symbol is σ , although $\tilde{\nu}$ is sometimes seen. In SI units, wavenumber would be expressed in m^{-1} , although cm^{-1} is often used. The extraordinary illiteracy "a line of 15376 wavenumbers" is heard regrettably often. What is intended is presumably "a line of wavenumber 15376 cm^{-1} ." The kayser was an unofficial unit formerly seen for wavenumber, equal to 1 cm^{-1} . As some wag once remarked: "The Kaiser (kayser) is dead!"

It is customary to quote wavelengths below 200 nm as wavelengths *in vacuo*, but wavelengths above 200 nm in "standard air". Wavenumbers are usually quoted as wavenumbers *in vacuo*, whether the wavelength is longer or shorter than 200 nm. Suggestions are made from time to time to abandon this confusing convention; in any case it is incumbent upon any writer who quotes a wavelength or wavenumber to state explicitly whether s/he is referring to a vacuum or to standard air, and not to assume that this will be obvious to the reader. Note that, in using the formula $n_1\lambda_1 = n_2\lambda_2 = n_3\lambda_3$ used for overlapping orders, the wavelength concerned is neither the vacuum nor the standard air wavelength; rather it is the wavelength in the actual air inside the spectrograph.

If I use the symbols λ_0 and σ_0 for vacuum wavelength and wavenumber and λ and σ for wavelength and wavenumber in standard air, the relation between λ and σ_0 is

$$\lambda = \frac{1}{n\sigma_0} \quad (7.1.1)$$

"Standard air" is a mythical substance whose refractive index n is given by

$$(n - 1) \cdot 10^7 = 834.213 + \frac{240603.0}{130 - \sigma_0^2} + \frac{1599.7}{38.9 - \sigma_0^2}, \quad (7.1.2)$$

where σ_0 is in μm^{-1} . This corresponds closely to that of dry air at a pressure of 760 mm Hg and temperature 15°C containing 0.03% by volume of carbon dioxide.

To calculate λ given σ_0 is straightforward. To calculate σ_0 given λ requires iteration. Thus the reader, as an exercise, should try to calculate the vacuum wavenumber of a line of standard air wavelength 555.5 nm. In any case, the reader who expects to be dealing with wavelengths and wavenumbers fairly often should write a small computer or calculator program that allows the calculation to go either way.

Frequency is the number of waves per second, and is expressed in hertz (Hz) or MHz or GHz, as appropriate. The usual symbol is ν , although f is also seen. Although wavelength and wavenumber change as light moves from one medium to another, frequency does not. The relation between frequency, speed and wavelength is

$$c = \nu\lambda_0 \quad (7.1.3)$$

where c is the speed *in vacuo*, which has the defined value $2.997\,924\,58 \times 10^8\text{ m s}^{-1}$.

A spectrum line results from a transition between two energy levels of an atom. The frequency of the radiation involved is related to the difference in energy levels by the familiar relation

$$h\nu = \Delta E, \quad (7.1.4)$$

where h is Planck's constant, $6.626075 \times 10^{-34}\text{ J s}$. If the energy levels are expressed in joules, this will give the frequency in Hz. This is not how it is usually done, however. What is usually tabulated in energy level tables is $E/(hc)$, in units of cm^{-1} . This quantity is known as the *term value* T of the level. Equation 7.1.4 then becomes

$$\sigma_0 = \Delta T \quad (7.1.5)$$

Thus the vacuum wavenumber is simply the difference between the two tabulated term values.

In some contexts it may also be convenient to express energy levels in electron volts, 1 eV being $1.60217733 \times 10^{-19}$ J. Energy levels of neutral atoms are typically of the order of a few eV. The energy required to ionize an atom from its ground level is called the *ionization energy*, and its SI unit would be the joule. However, one usually quotes the ionization energy in eV, or the *ionization potential* in volts.

It may be remarked that sometimes one hears the process of formation of a spectrum line as one in which an "electron" jumps from one energy level to another. This is quite wrong. It is true that there is an adjustment of the way in which the electrons are distributed around the atomic nucleus, but what is tabulated in tables of atomic energy levels or drawn in energy level diagrams is the energy of the *atom*, and in equation 7.1.4 ΔE is the change in energy of the *atom*. This includes the kinetic energy of all the particles in the atom as well as the mutual potential energy between the particles.

We have seen that the wavenumber of a line is equal to the difference between the term values of the two levels involved in its formation. Thus, if we know the term values of two levels, it is a trivial matter to calculate the wavenumber of the line connecting them. In spectroscopic analysis the problem is very often the converse - you have measured the wavenumbers of several spectrum lines; can you from these calculate the term values of the levels involved? For example, here are four (entirely hypothetical and artificially concocted for this problem) vacuum wavenumbers, in μm^{-1} :

1.96643
2.11741
2.28629
2.43727

The reader who is interested on spectroscopy, or in crossword puzzles or jigsaw puzzles, is very strongly urged to calculate the term values of the four levels involved with these lines, and to see whether this can or cannot be done without ambiguity from these data alone. Of course, you may object that there are six ways in which four levels can be joined in pairs, and therefore I should have given you the wavenumbers of six lines. Well, sorry to be unsympathetic, but perhaps two of the lines are too faint to be seen, or they may be forbidden by selection rules, or their wavelengths might be out of the range covered by your instrument. In any case, I have told you that four levels are involved, which is more information that you would have if you had just measured the wavenumbers of these lines from a spectrum that you had obtained in the laboratory. And at least I have helped by converting standard air wavelengths to vacuum wavenumbers. The exercise will give some appreciation of some of the difficulties in spectroscopic analysis.

In the early days of spectroscopy, in addition to flames and discharge tubes, common spectroscopic sources included arcs and sparks. In an arc, two electrodes with a hundred or so volts across them are touched, and then drawn apart, and an arc forms. In a spark, the potential difference across the electrodes is some thousands of volts, and it is not necessary to touch the electrodes together; rather, the electrical insulation of the air breaks down and a spark flies from one electrode to the other. It was noticed that the arc spectrum was usually very different from the spark spectrum, the former often being referred to as the "first" spectrum and the latter as the "second" spectrum. If the electrodes were, for example, of carbon, the arc or first spectrum would be denoted by C I and the spark or second spectrum by C II. It has long been known now that the "first" spectrum is mostly that of the neutral atom, and the "second" spectrum mostly that of the singly-charged ion. Since the atom and the ion have different electronic structures, the two spectra are very different. Today, we use the symbols C I, or Fe I, or Zr I, etc., to denote the spectrum of the neutral atom, regardless of the source, and C II, C III, C IV, etc., to denote the spectra of the singly-, doubly- triply-ionized atoms, C^+ , C^{++} , C^{+++} , etc. There are 4278 possible spectra of the first 92 elements to investigate, and many more if one adds the transuranic elements, so there is no want of spectra to study.

Hydrogen, of course, has only one spectrum, denoted by H I, since ionized hydrogen is merely a proton. The regions in space where hydrogen is mostly ionized are known to astronomers as "H II regions". Strictly, this is a misnomer, for there is no "second spectrum" of hydrogen, and a better term would be " H^+ regions", but the term "H II regions" is by now so firmly entrenched that it is unlikely to change. It is particularly ironic that the spectrum exhibited by an "H II region" is that of neutral hydrogen (e.g. the well-known Balmer series), as electrons and protons recombine and drop down the energy level ladder. On the other hand, apart from the 21 cm line in the radio region, the excitation temperature in regions where hydrogen is mostly neutral (and hence called, equally wrongly, "H I regions") is far too low to show the typical spectrum of neutral hydrogen, such as the Balmer series. Thus it can be accurately said that "H II regions" show the spectrum of H I, and "H I regions" do not. Lest it be thought that this is

unnecessary pedantry, it should be made clear at the outset that the science of spectroscopy, like those of celestial mechanics or quantum mechanics, is one in which meticulous accuracy and precision of ideas is an absolute necessity, and there is no room for vagueness, imprecision, or improper usage of terms. Those who would venture into spectroscopy would do well to note this from the beginning.

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