

## Appendix

A full description of the phenomena illustrated by light sources shown in Figures 2–7 requires the use of concepts generally introduced in upper division physical chemistry. Included below are more detailed explanations of the theory behind the output and operation of these sources that may be used in adapting the experiment for the physical chemistry laboratory.

The Planck distribution law for blackbody radiation in terms of wavelength is given by the expression [1]

$$d\rho(\lambda, T) = \rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\exp(hc / \lambda k_b T) - 1} \quad (1)$$

where the quantity  $\rho_\lambda(T)d\lambda$  is the radiant energy density between  $\lambda$  and  $\lambda + d\lambda$ . Prior to Planck's derivation of this law, Wien empirically deduced the relationship

$$\lambda_{\max} T = 2.90 \times 10^{-3} \text{ m} \cdot \text{K} \quad (2)$$

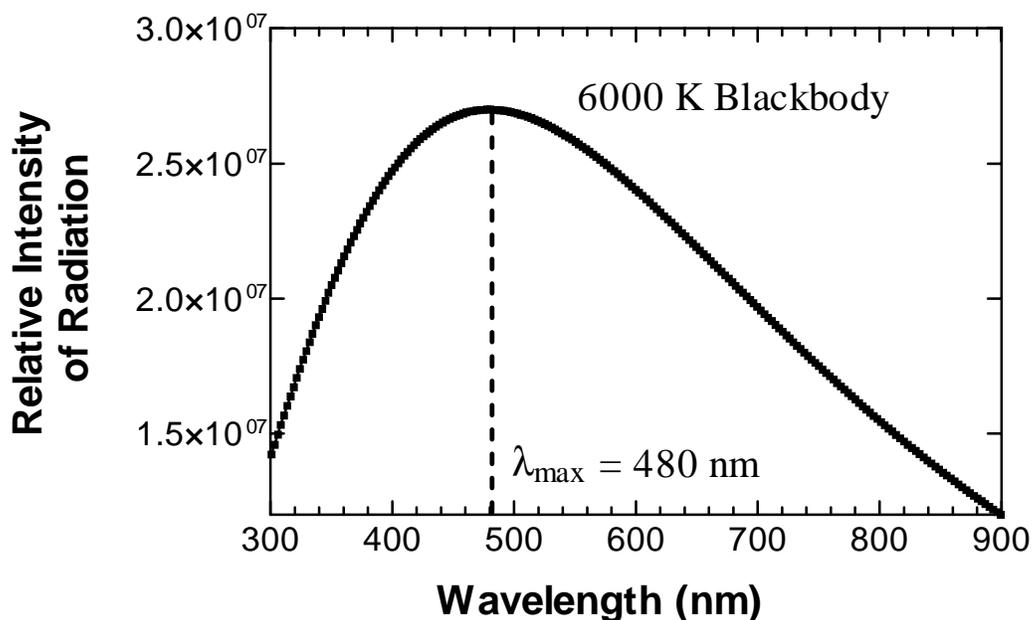
which can be obtained by differentiating (1) with respect to wavelength and solving the result numerically [1]. In the field of radiometry, Planck's law is generally expressed in units of spectral irradiance or radiant exitance, Watts per meter squared per unit wavelength,  $\text{W} \cdot \text{m}^{-2} \cdot \mu\text{m}^{-1}$ . In Figure 1, the spectral irradiance is plotted versus wavelength according to the relationship

$$M = \frac{c_1}{\lambda^5 [\exp(c_2 / \lambda T) - 1]} \quad (3)$$

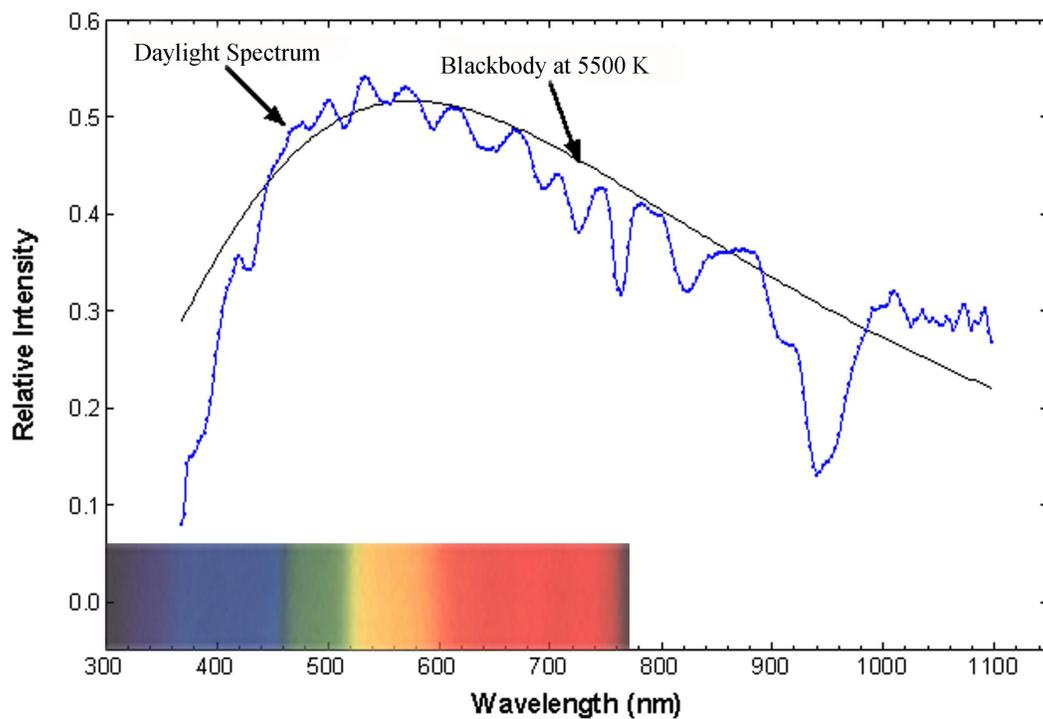
where  $M$  is the spectral irradiance,  $c_1$  is the first radiation constant ( $c_1 = 2\pi^5 hc^2 / 15 = 3.7418 \times 10^8 \text{ W} \cdot \mu\text{m}^4 \cdot \text{m}^{-2}$ ) and  $c_2$  is the second radiation constant ( $c_2 = hc/k = 14,388 \mu\text{m} \cdot \text{K}$ ) [2].

## Solar/Daylight Spectral Distribution

The spectral distribution of daylight collected near sea level (Figure 2) maintains the same general shape of a blackbody radiating near 5500 K, but deviates from that of a blackbody for several reasons, most noticeably because of atmospheric extinction.



**FIGURE 1.** SPECTRUM OF A BLACKBODY RADIATOR AT 6000 K. THE WAVELENGTH CORRESPONDING TO THE MAXIMUM OF THE CURVE CAN BE DETERMINED USING WIEN'S LAW.



**FIGURE 2.** SPECTRUM OF DAYLIGHT (BLUE CURVE) FIT TO A 5500 K PLANCK BLACKBODY DISTRIBUTION FUNCTION.

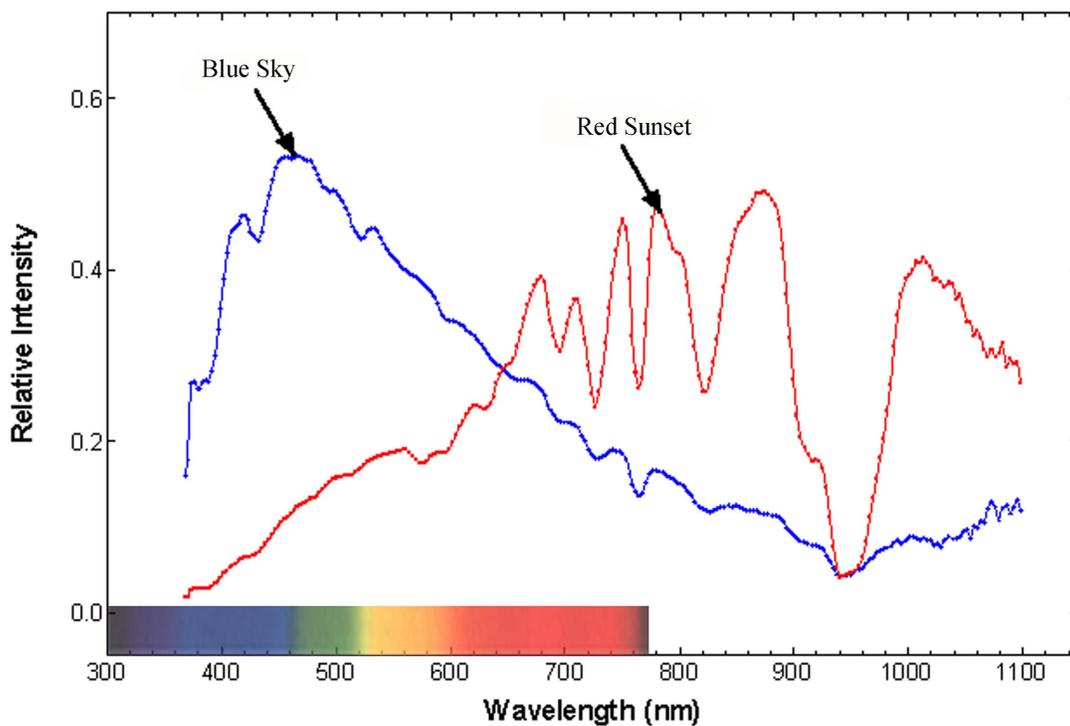


FIGURE 3. COMPARISON SPECTRUM OF BLUE SKY TO RED SUNSET.

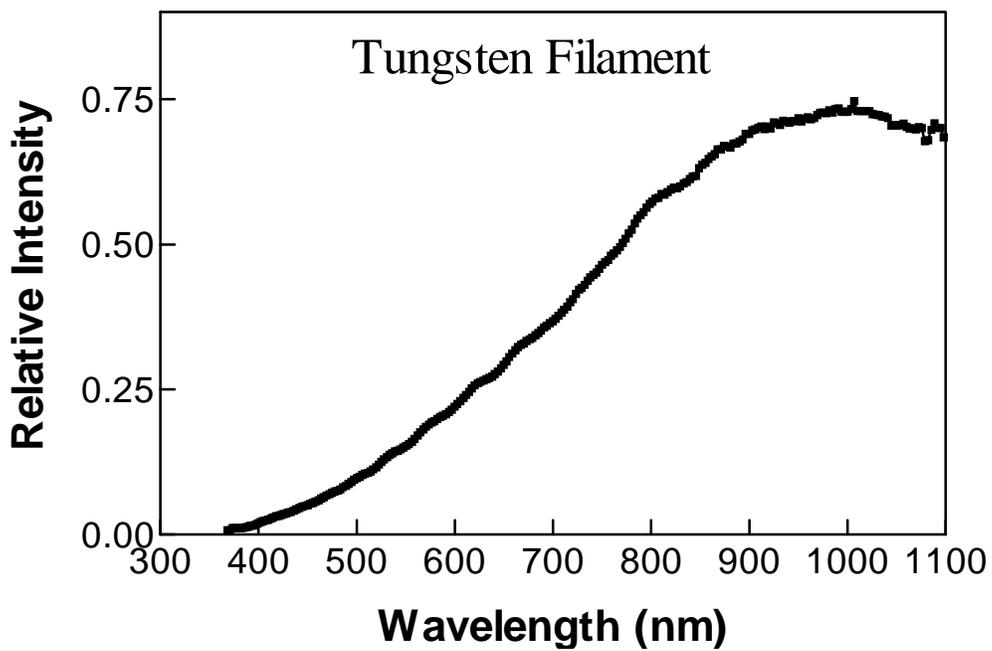
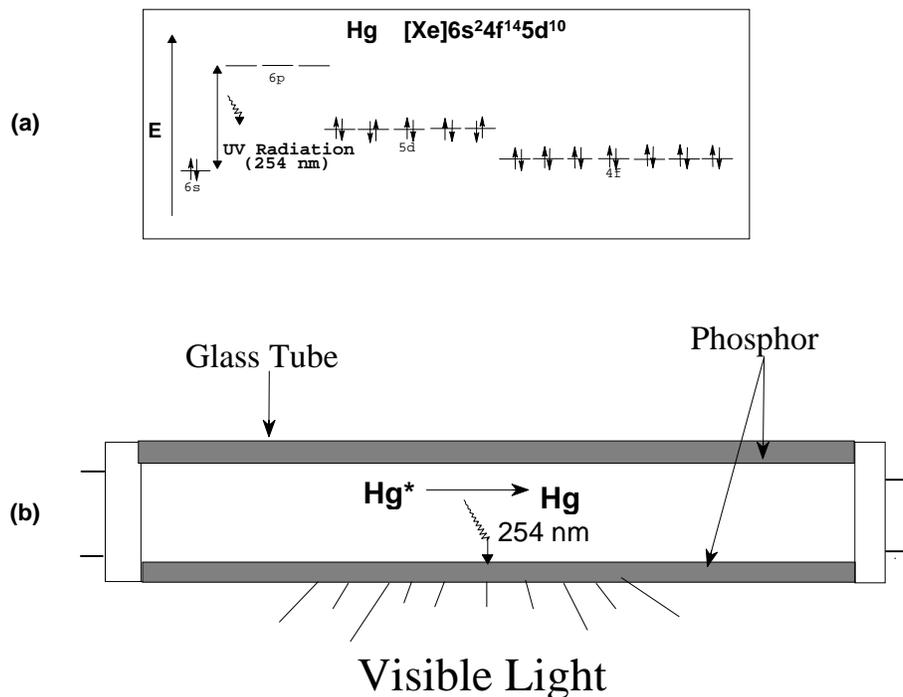
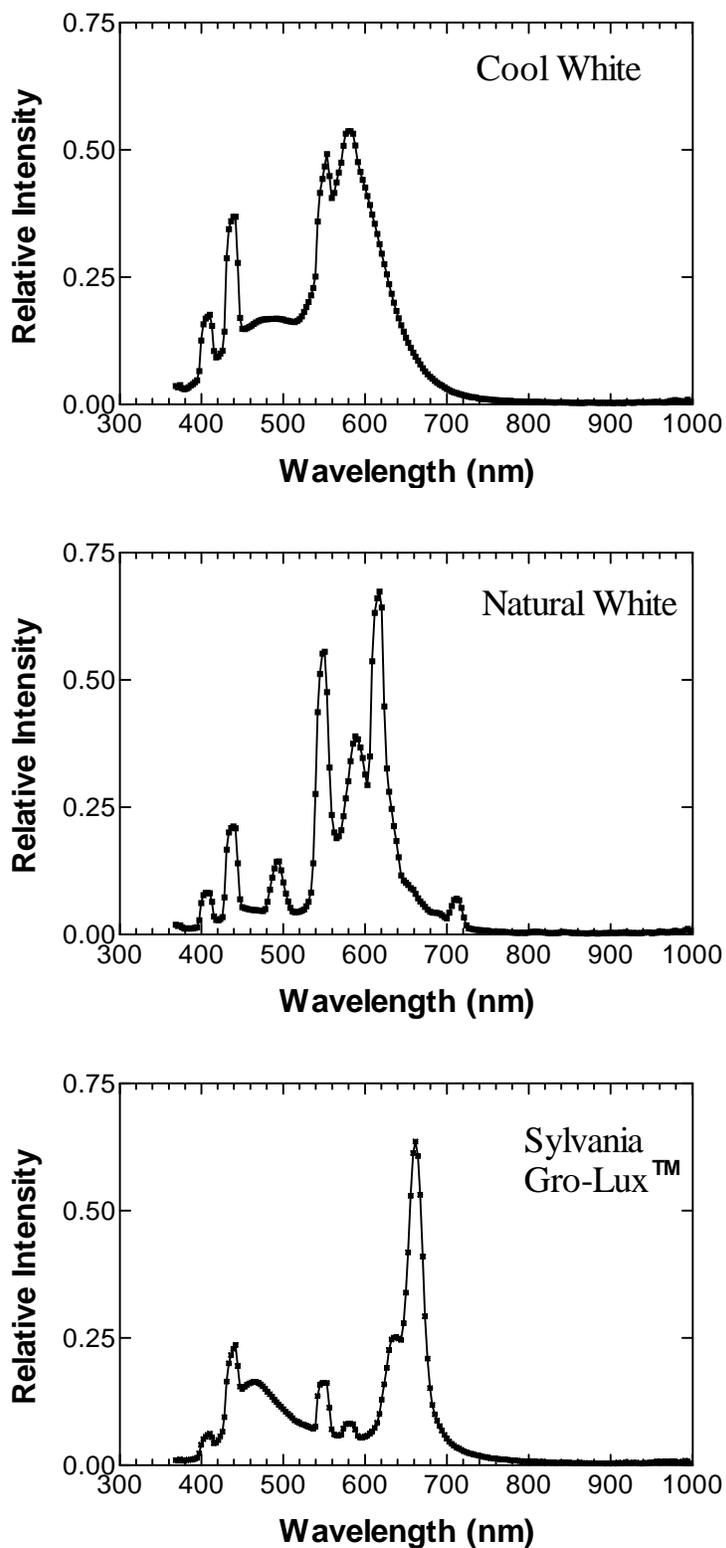


FIGURE 4. SPECTRUM OF A TUNGSTEN FILAMENT WITHIN A WHITE LIGHT BULB.



**FIGURE 5.** (A) PARTIAL ENERGY LEVEL DIAGRAM FOR Hg. (B) SCHEMATIC DIAGRAM OF A FLUORESCENT LAMP AND ITS OPERATION. SEE TEXT.

The spectrum of the solar radiation reaching the Earth's surface depends not only on solar altitude but on the local albedo, or reflectance of the radiation by its surroundings [3]. Radiation reaching the spectroradiometer's camera passes through the atmosphere which modifies the spectrum by absorption and scattering. Molecular nitrogen and oxygen absorb UV radiation below 190 nm, and when molecular oxygen absorbs this short wavelength radiation, it photodissociates. The photodissociation of oxygen leads to the formation of ozone, which absorbs strongly in the UV from 200–360 nm (Hartley and Huggins bands), and weakly in the visible region from 450–750 nm (Chappius bands) [3]. The ozone layer “cuts off” the UV radiation reaching the troposphere sharply near 290 nm, thus defining the beginning of the solar spectrum. Water vapor and oxygen are responsible for absorptions shown in Figure 2 from 700–1100 nm. A detailed description of the spectral positions, intensities and bandwidths of atmospheric gases absorbing in the near IR portion of the solar spectrum can be found in reference 4.



**FIGURE 6.** SPECTRA OF THREE DIFFERENT TYPES OF FLUORESCENT LAMPS: COOL WHITE, NATURAL WHITE, AND GRO-LUX™.

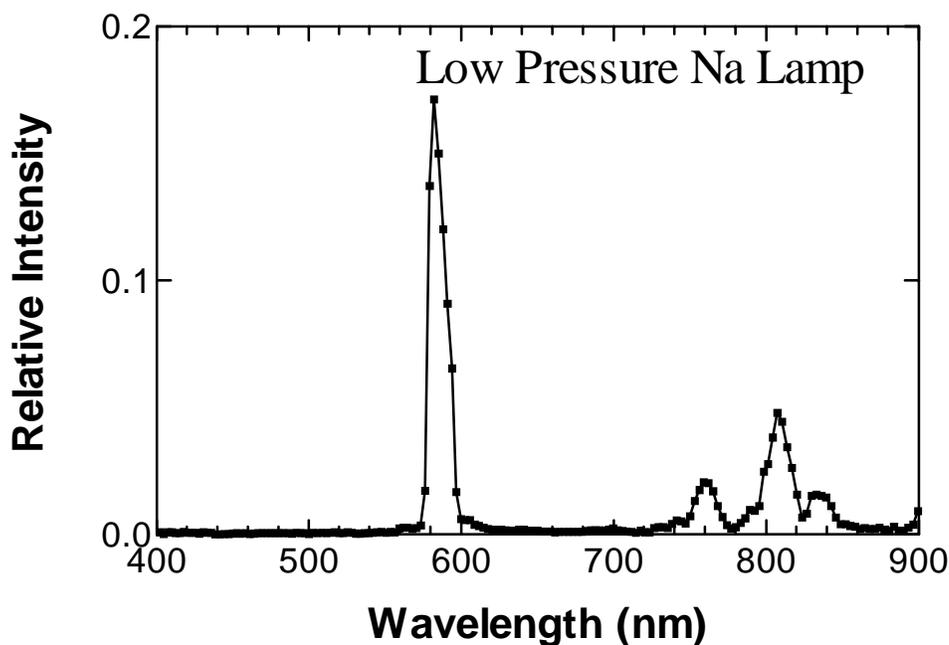


FIGURE 7. SPECTRUM OF A LOW-PRESSURE SODIUM VAPOR LAMP.

The extraterrestrial solar spectrum more closely approximates that of a blackbody; solar surface temperatures near 6000 K have been reported [5]. Other stars are characterized by their color temperature as well. For example, Epsilon Orionis and Sirius, with surface temperatures of 28,000 K and 13,600 K, respectively, are blue-white stars, and Betelgeuse (3600 K) is a red star [6].

### Tungsten Lamp

Among the light sources studied in this project, the filament lamp's spectral distribution best approximates that of a blackbody radiator. The filament temperature in a tungsten light bulb generally ranges from 2800–3200 K with greater luminosities achieved at higher temperatures [7]. Unfortunately, as the filament temperature is increased, the rate of its evaporation increases, leading to a shorter lifetime of the bulb due to bulb darkening. To reduce the evaporation of the filament, an inert gas, or a mixture of inert gases, is added to the bulb. The inert gas inhibits the transport of tungsten vapor from the filament; strictly speaking, it decreases the mean free path of a gaseous tungsten atom. Generally, tungsten lamps are filled with 90% argon and 10% nitrogen to a pressure somewhat below 1 atm [7]. The presence of the nitrogen is

necessary to prevent arcing between the ends of the filament which would occur if pure Ar was used.

Longer lamp life and increased efficacy are achieved in the tungsten-halogen lamp, or halogen bulb, which adds a halogen to the filling gas and utilizes a reversible chemical reaction between the tungsten and the halogen. For example, if iodine, or a molecule containing iodine, is added to the bulb, the reaction  $W + 2I \rightleftharpoons WI_2$  occurs within a specific temperature zone (near 1000 °C) between the hot filament and the bulb wall. In halogen lamps, the evaporated tungsten is returned to the filament by a chemical transport process, which prevents blackening of the bulb. The tungsten iodide molecules diffuse towards the filament where they dissociate, and the tungsten can be deposited back onto the filament, leaving the halogen available for another reaction cycle. Reactive gases such as HI, HBr, CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, CH<sub>3</sub>Br and NF<sub>3</sub> are typically used in halogen lamps to generate tungsten transport cycles [7]. The regenerative cycle allows a higher filament temperature to be used; temperatures from 2400–3250 °C are typical (the melting point of W is 3410 °C) [7]; thus, the spectral distributions of the tungsten-halogen lamps are similar to that of a tungsten lamp (see Figure 4), except that their maxima are shifted toward the UV region. Common uses of halogen lamps include slide/overhead projectors, automobile headlights, and floodlighting in outdoor sporting arenas.

## Gas Discharges

### *Fluorescent Lamp*

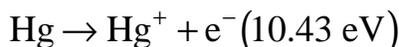
In a low-pressure discharge lamp, such as a fluorescent lamp, ionization is primarily caused by electron impact. The radiation produced depends upon the energy imparted to the atoms and their available energy states; thus, the study of gas discharges provides a convenient means to introduce Grotrian diagrams in physical chemistry. A partial energy-level diagram for mercury is shown in Figure 8; complete Grotrian diagrams for many elements can be found in Herzberg [8].

The region of the discharge between the electrodes in a gas-discharge lamp is called the positive column and consists of a mixture of gaseous atoms, ions and electrons [7]. In the discharge of a fluorescent lamp, which contains mercury and argon, almost all of the ions produced are mercury ions resulting from collisions of neutral Hg atoms with the more energetic electrons in the discharge. Because the ionization energy of Hg

(10.43 eV) is less than that of Ar (15.76 eV), ionization of Hg occurs preferentially [7]. Furthermore, if some Ar atoms are excited to a metastable energy state below its ionization limit, they then can transfer their excitation energy to Hg through a collision. This collisional energy transfer will result in the ionization of a Hg atom if the energy of the metastable state of Ar is greater than the ionization potential of Hg.



In this example, Ar has a metastable state ( $^3\text{S}$ ) which is 11.55 eV above its ground state and higher in energy than the ionization potential of Hg (10.43 eV).

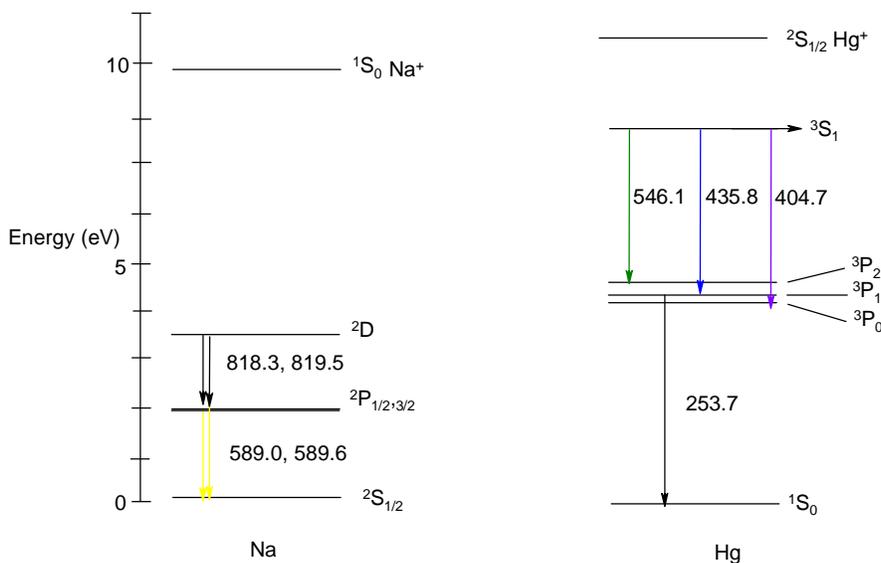


This phenomenon is known as Penning ionization [9] and is used in other types of discharge lamps as well. The use of this type of Penning mixture enables the voltage which is initially applied to the electrodes to be reduced.

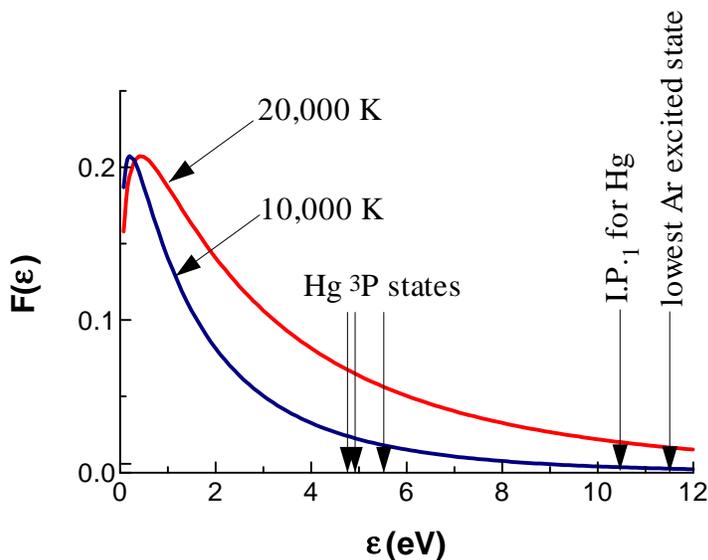
The kinetic energy of the electrons produced in the low pressure discharge is characterized approximately by a Maxwell-Boltzmann distribution function

$$F(\varepsilon)d\varepsilon = \frac{2\pi}{\pi k_B T^{3/2}} \varepsilon^{1/2} \exp(-\varepsilon / k_B T) d\varepsilon \quad (4)$$

where  $\varepsilon$  is the kinetic energy and  $T$  is the absolute temperature [1]. Applied to the electrons in a discharge lamp,  $T$  corresponds to the electron temperature. Figure 9 shows the Maxwell-Boltzmann distribution for electron temperatures (10,000 and 20,000 K) typically found in a fluorescent lamp. Also shown are the energies of relevant atomic states for Hg and Ar. At a temperature of 10,000 K, a small fraction of electrons possess energies necessary to ionize Hg, and at 20,000 K this fraction of electrons is greater. At either electron temperature, a much greater fraction of electrons has enough energy to excite mercury atoms than have sufficient energy to excite argon atoms. In a fluorescent lamp, over 50% of the input power is radiated at 253.7 nm ( $^3\text{P}_1 \rightarrow ^1\text{S}_0$ , 4.89 eV) [7]. Although this transition is not strictly allowed according to the selection rules  $\Delta L = 0, \pm 1$ ,  $\Delta S = 0$ , the large spin-orbit coupling in Hg breaks down these selection rules making the transition possible [1].



**FIGURE 8.** PARTIAL ENERGY-LEVEL DIAGRAMS FOR SODIUM AND MERCURY. ONLY THE PRINCIPAL LEVELS RELEVANT TO THE LOW-PRESSURE DISCHARGE LAMPS ARE SHOWN.



**FIGURE 9.** MAXWELL-BOLTZMANN DISTRIBUTION FOR ELECTRON TEMPERATURES TYPICAL OF THOSE FOUND IN A FLUORESCENT LAMP. ALSO SHOWN FOR COMPARISON ARE THE ENERGIES OF SOME RELEVANT STATES OF MERCURY AND ARGON.

### *Sodium Vapor Lamp*

As in the fluorescent lamp, atoms in the sodium lamp are excited and ionized by electron impact. In addition to the sodium metal, a mixture of inert gases is necessary to initiate and optimize the discharge lamp. The usual inert gas mixture in a low

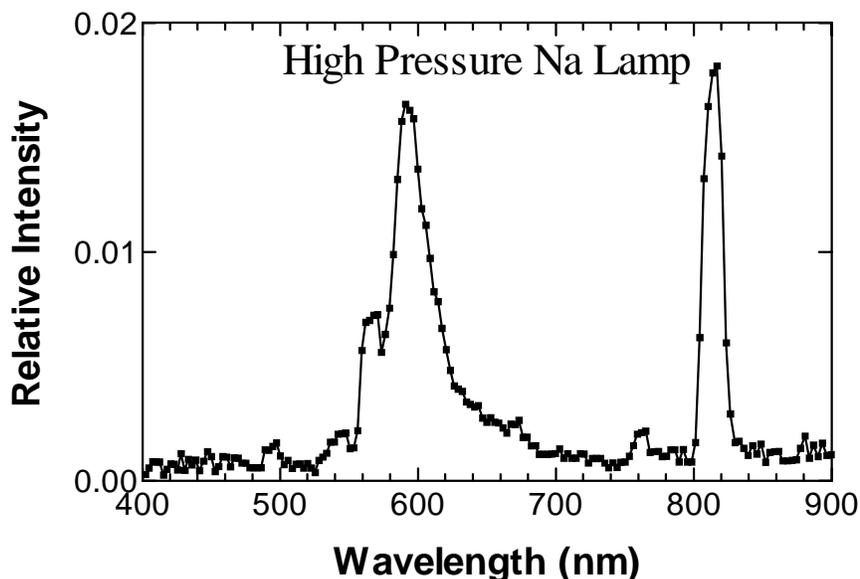


FIGURE 10. SPECTRUM OF A HIGH-PRESSURE SODIUM VAPOR LAMP. SEE FIGURE 7 FOR COMPARISON.

pressure sodium lamp is 99% neon and 1% argon (Penning mixture) [10]. Visible radiation is provided by the relaxation of excited  $^2P_{3/2}$  or  $^2P_{1/2}$  Na atoms to the ground state (Figure 8). Due to the limited resolution of our spectroradiometer, the sodium D lines (589.0 and 589.6 nm) emitted by the low-pressure Na lamp are not resolved (see Figure 7).

High-pressure Na-vapor lamps, also used in outdoor lighting, contain higher pressures of mercury (400–800 torr) and xenon (150–200 torr) and exhibit a broader spectrum, due primarily to collisional broadening (Figure 10). The more continuous nature of the high-pressure lamp's spectrum results in better color rendering. The resolution of our spectroradiometer does not permit a quantitative investigation of the self-absorption of the D lines that occurs in the high-pressure lamp [11]. High-pressure Na lamps are used in road/highway lighting and, because of their improved color rendering over the low-pressure lamps, they are also used in security lighting.

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