

Thermodynamics of daylight-pumped lasers

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We cast the problem of very-low-threshold, daylight-pumped lasers in a general thermodynamic framework. We calculate that the requirements to reach threshold are that the Stokes shift of such a laser be greater than $13.3kT$ and that the absorption ratio of the pump/emission band and the geometrical aspect ratio both be greater than $\exp(13.3)$. We describe some luminescent material systems that might be able to satisfy these rigid requirements.

Of all laser-excitation mechanisms, optical pumping was the first and remains the most common. On a clear day, the sun is a bright pump source. When strongly focused, sunlight is quite capable of producing cw lasing, as has been demonstrated in Nd:YAG, for example.¹ In this Letter we determine the requirements for a laser that can be pumped by *unfocused* sunlight, i.e., daylight. A daylight-pumped laser would not require any mechanical contrivance to track the sun's motion and would operate even on cloudy days. Such a laser might have practical importance as a high-concentration-ratio nontracking solar collector.

The technical challenge of a daylight-pumped laser is severe, however. Only 100 mW/cm² of broadband radiation is available from daylight. Achieving gain under such conditions is not now feasible with known lasing media. Our purpose in this Letter is to cast the problem in a general thermodynamic framework. This can guide further materials research without necessarily prejudging which technical path is most likely to succeed. In this spirit, we take the absorption and/or luminescence spectrum of the lasing medium to be completely adjustable. We seek to determine which constraints the absorption spectrum must satisfy in order to permit daylight-pumped lasing thermodynamically.

We employ a model of the luminescent medium that was first developed many years ago by Kennard² for dye molecules and has since been applied to photochemical³ and semiconductor^{4,5} systems. In this approach, the material is considered to be made up of an electronically excited band and a ground-state band. The key assumption is that relaxation inside each of the bands is fast compared with interband relaxation so that thermal equilibrium is reached inside each band. This approximation is valid in dye and most semiconductor systems and is often good in atomic or solid-state lasers as well. Fast intraband relaxation is also the best possible situation for achieving laser action.

To determine the gain spectrum of an arbitrary medium in terms of its absorption spectrum, we follow the approach used by Ross³ and Henry.⁵ If an excited medium is in equilibrium with a radiation field, absorption of a photon will reduce the entropy of the field, which must be balanced by a corresponding increase in

entropy of the medium. The change in entropy of the field⁶ that is due to loss of one photon is

$$\Delta S = -k \ln \left(1 + \frac{8\pi n^2 \nu^2}{c^2 B} \right).$$

The corresponding increase in entropy of the medium that is due to the uptransition is

$$\Delta S = (h\nu - \mu)/T,$$

where μ , the free energy, is nonzero because the medium is already highly electronically excited. B , the brightness of the field, is given in photons per unit area, per unit bandwidth, per unit time, and per 4π solid angle. Here T is the ambient temperature, n is the index of refraction, and ν is the optical frequency. Balancing the entropy changes, the brightness of the radiation field that is in equilibrium with the electronic transition of the medium is

$$B(\nu, \mu, T) = \frac{8\pi n^2 \nu^2}{c^2} \left[\exp \left(\frac{h\nu - \mu}{kT} \right) - 1 \right]^{-1}. \quad (1)$$

For the situation in which there is no electronic excitation of the medium, i.e., $\mu = 0$, Eq. (1) reduces to the ambient-temperature Planck distribution, as it should.

Consider the radiative equilibrium from the viewpoint of the medium. Its net rate of uptransition per unit volume should exactly balance its rate of spontaneous emission $L(\nu, \mu, T)$ at each frequency. This is the well-known principle of detailed balance:

$$L(\nu, \mu, T) = \alpha(\nu, \mu, T)B(\nu, \mu, T). \quad (2)$$

Therefore the absorption spectrum may be written as

$$\alpha(\nu, \mu, T) = L(\nu, \mu, T) \frac{c^2}{8\pi n^2 \nu^2} \left[\exp \left(\frac{h\nu - \mu}{kT} \right) - 1 \right]. \quad (3)$$

Since the luminescent emission spectrum L is positive definite, the absorption coefficient α becomes a gain coefficient for photon energies $h\nu$ less than the chemical potential μ . This is known as the Bernard-Duraffourg condition⁷ in the semiconductor context. We have followed the derivation given by Ross.³ Henry⁵ first

showed that Eq. (3) accurately describes the gain spectra of semiconductor lasers.

Equation (2), which dates back to Kennard,² connects the absorption and luminescent spectra. In the limit of weak excitation, $h\nu \gg \mu$, the luminescent spectrum has frequently been written in the following form:

$$L(\nu, \mu, T) = \alpha(\nu, 0, T) \frac{8\pi n^2 \nu^2}{c^2} \exp\left(\frac{\mu - h\nu}{kT}\right). \quad (4)$$

Under weak excitation, the luminescence spectrum follows the unpumped absorption coefficient $\alpha(\nu, 0, T)$. In addition, we are permitted to ignore stimulated emission and drop the one from the Bose denominator in Eq. (3). When applied to semiconductors, Eq. (4) is known as the van Roosbroeck-Shockley relation.⁴ In that case, the chemical potential μ is the separation of quasi-Fermi levels for electrons and holes.

When a material is highly excited, its luminescence spectrum does not necessarily experience a drastic change in shape. In fact, Eq. (4) does a reasonably good job of describing luminescent emission in many cases, even when $h\nu \approx \mu$. It is not accurate in a case in which the absorption and the gain begin to saturate because of the filling of states. For example, in the case of a two-level system, Eq. (4) will overestimate L by a factor of 2 when $h\nu \approx \mu$. It also does not hold in a semiconductor pumped to the point of degeneracy but will cover near-threshold lasing in a highly doped semiconductor.

If gain saturation does not occur, Eq. (4) will generally be accurate as long as a high excitation density does not result in the onset of new physical processes, such as carrier screening in semiconductors. Equation (4) is particularly valid in our context since we are considering weakly pumped lasers. Therefore we substitute Eq. (4) into Eq. (3) to obtain the net absorption coefficient

$$\alpha(\nu, \mu, T) = \alpha(\nu, 0, T) \left[1 - \exp\left(\frac{\mu - h\nu}{kT}\right) \right]. \quad (5)$$

Equation (5) will be useful for us since it describes the expected gain spectrum in terms of a given absorption spectrum. The only unknown on the right-hand side of Eq. (5) is the chemical potential μ , which is determined by the balance between pumping rates and deexcitation rates. The problem of the low-threshold lasing then reduces to making $\mu > h\nu_L$ at a lasing frequency ν_L for which $\alpha(\nu_L, 0, T) \equiv \alpha_L$ is sufficiently large.

It is our purpose to determine what shape for the absorption spectrum would produce an optimal low-threshold laser. Let us specialize to the spectral shape indicated in Fig. 1. The lasing will take place from a narrow band of width $\Delta\nu_L$ centered on ν_L . A narrow band is desired here to minimize spontaneous emission. The pumping will be into a broad flat band with absorption coefficient α_a , which falls steeply from a band edge at ν_a . Thermal equilibrium between these two bands is assumed. Our purpose then is to determine the necessary conditions on ν_L , ν_a , α_L , α_a , and $\Delta\nu_L$.

In a steady state the excitation process is balanced by the energy-loss process. In an optically pumped laser, the excitation is by light, and the loss processes are by spontaneous and stimulated emission as well as by

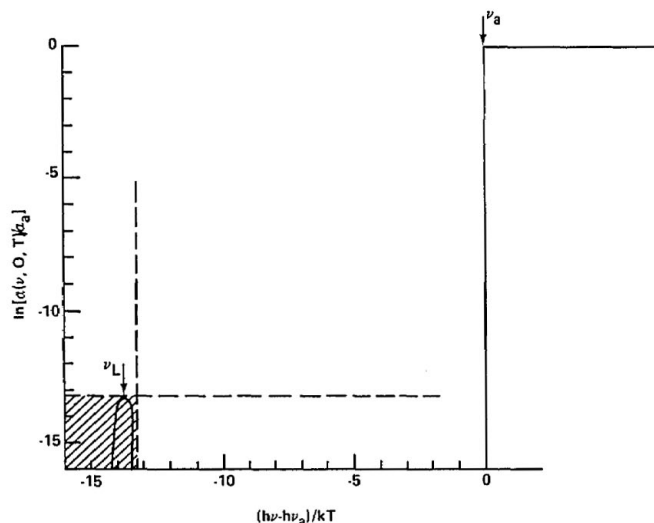


Fig. 1. The absorption spectrum thermodynamically required of a very-low-threshold daylight-pumped lasing medium. The laser line must be in the shaded region, sufficiently lower in energy and of considerably lower absorption coefficient than the emission line. After excitation the emission line absorption becomes inverted in accordance with Eq. (5).

nonradiative mechanisms. It is the balance between these competing rates that determines the chemical potential μ . Since we are considering the threshold condition for lasing, let us neglect the effect of stimulated emission on the level populations, which becomes important only well above threshold. As an additional simplification let us express the effect of nonradiative decay in terms of a constant quantum efficiency η , which is less than unity. Then the main decay mechanism that we must be concerned with is spontaneous emission. We know that this is inescapable since absorption and spontaneous emission are thermodynamically linked.

The overall luminescent emission rate per unit volume is the integral over all frequencies of Eq. (4). There will be spontaneous emission from both the lasing line ν_L and the absorption band edge at ν_a .

The luminescence intensity from the absorption band should be less than the pump rate per unit volume:

$$\alpha_a \frac{kT}{h} \frac{8\pi n^2 \nu_a^2}{c^2} \exp\left(\frac{\mu - h\nu_a}{kT}\right) < \eta \alpha_a I_p, \quad (6)$$

where I_p is the pump intensity in photons per square centimeters per second. Here we have assumed that ν^2 is slowly varying compared with the exponential term in the integral. The amount of luminescence does not depend critically on the shape of the absorption band, as long as the band edge falls off faster than $\exp(h\nu/kT)$ for $\nu < \nu_a$. Expression (6) can be rewritten to show that the Stokes shift from absorption band edge to the lasing energy must be at least

$$h\nu_a - \mu > kT \ln\left(\frac{8\pi n^2 \nu_a^2 kT}{c^2 \eta I_p h}\right). \quad (7)$$

The luminescence from ν_L (at the gain threshold $\mu \approx h\nu_L$) should also be less than the pump rate:

$$\alpha_L \Delta\nu_L \frac{8\pi n^2 \nu_L^2}{c^2} < \eta \alpha_a I_p, \quad (8)$$

where $\Delta\nu_L = \int \alpha(\nu, 0, T) d\nu / \alpha_L$ is the width of the absorption band. Therefore the absorption at α_L must be sufficiently weak:

$$\frac{\alpha_a}{\alpha_L} > \frac{8\pi n^2 \nu_L^2 \Delta\nu_L}{c^2 \eta I_p}. \quad (9)$$

An important role in expressions (7) and (9) is played by the large dimensionless number $N \equiv 8\pi n^2 \nu_a^2 kT / c^2 \eta I_p h$, which measures the weakness of the pump source. Using $h\nu_a = 1.4$ eV and $I_p = 2 \times 10^{17}$ photons/cm² sec, which are characteristic of daylight, and assuming that $n = 2.5$, $\eta = 1$, and $T = 300$ K, we arrive at $N = 6 \times 10^5$. Then the minimum Stokes shift is $h\nu_a - h\nu_L = kT \ln N = 13.3kT$. The laser line must be at least $13.3kT \approx 0.33$ eV below the absorption edge $h\nu_a$, as indicated by the vertical dashed line in Fig. 1. Similarly, expression (9) shows that the ratio of absorption coefficients α_a/α_L should be at least $N(\nu_L^2/\nu_a^2)(h\Delta\nu_L/kT)$. If $(\nu_L^2/\nu_a^2)(h\Delta\nu_L/kT) = 1$, then $\alpha_a/\alpha_L \approx N = 6 \times 10^5$. Therefore the emission band α_L should be below the horizontal line in Fig. 1. So, to reach threshold, the emission line should fall in the shaded part of Fig. 1.

The absorption ratio α_a/α_L in expression (7) places an additional geometrical constraint on the design of a daylight-pumped laser. Efficient absorption requires $\alpha_a t \approx 1$, where t is the thickness of the medium. In addition, the length l of the medium should be of the order of the reciprocal gain $1/g_L$. But Eq. (5) shows that $g_L \approx \alpha_L$ for chemical potential μ just above threshold. Therefore the geometrical aspect ratio of the medium $l/t > \alpha_a/\alpha_L = N(\nu_L^2/\nu_a^2)(h\Delta\nu_L/kT)$, i.e., the aspect ratio would have to be upward of 10^4 , depending on the exact value of $\Delta\nu_L$. For a 1- μ m-thick absorber, the gain length might have to be as long as 1 m.

The main remaining question in this Letter is whether there exist any potential material systems that fall within the constraints of Fig. 1 and expressions (7) and (9). Semiconductors have nearly ideal absorption curves for the high-absorption part of the spectrum.

Pure semiconductors also have negligible absorption in the band gap. A natural method for providing the narrow emission line inside the gap is by doping.

Rare-earth dopants can provide narrow emission lines because they have incomplete inner shells that are isolated from the lattice. Narrow efficient room-temperature luminescence has been seen⁸ in CdS:Yb³⁺.

Another possibility for creating the desired absorption spectrum is an epitaxial-semiconductor sandwich structure. A thin narrow-gap layer could provide the stimulated emission and be sandwiched between two semiconductors whose gaps are at least $13.3kT$ larger. In this way the wide-gap material would absorb the incoming photons, transferring the excitation to the narrow-gap layer. The absorption spectrum of Fig. 1 (with a relatively broad emission band) could be synthesized in this way. It would be important, of course, to allow for quantum well effects on the carriers and waveguide effects on the photons, which would modify some of the formulas that we have given here. A similar multiple-layer structure was recently employed by Tsang⁹ to make very-low-threshold electrically pumped lasers.

In conclusion, we have outlined the necessary conditions for very-low-threshold daylight-pumped lasers. The Stokes shift must be greater than $13.3kT$. The absorption ratio of the pump/emission band as well as the geometrical aspect ratio must be $> \exp(13.3)$.

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