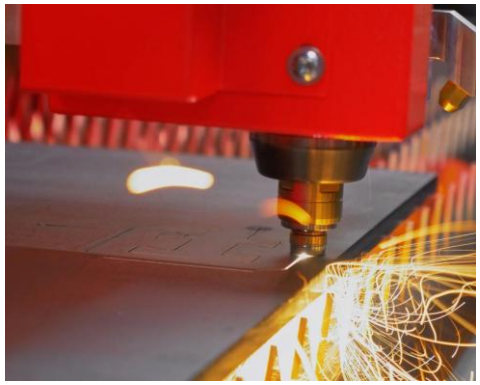
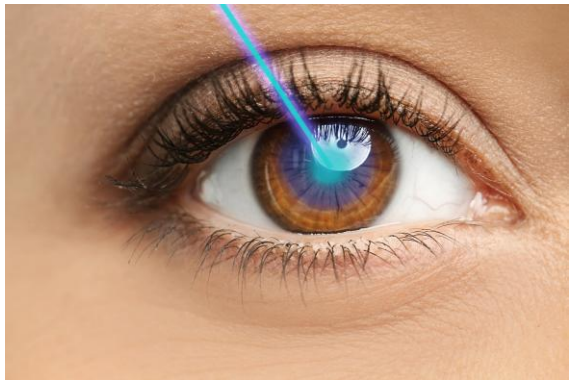
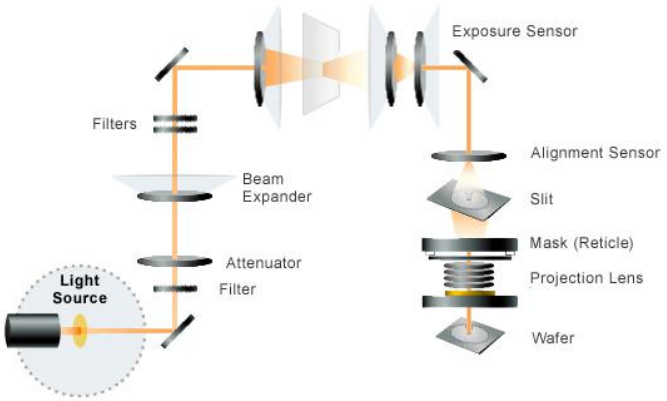
How Lasers Work (with examples)







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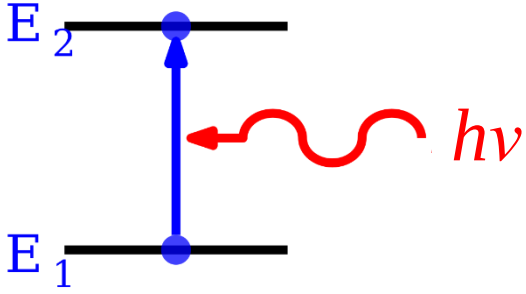
Einstein A and B coefficients

In 1916, Einstein proposed that there are three basic processes for the absorption and emission of electromagnetic radiation:

(1). Absorption – the atom or molecule absorbs radiation and is placed in an excited state. The rate is proportional to the intensity of the radiation at the wavelength of the transition.



Rate of absorption per molecule = $B_{2\leftarrow1}I(\omega_{21})$

The B coefficient tells how easy (or hard) it is to excite the molecule using electromagnetic radiation.

$B_{2\leftarrow1}I(\omega_{21})$ has units of s^{-1}

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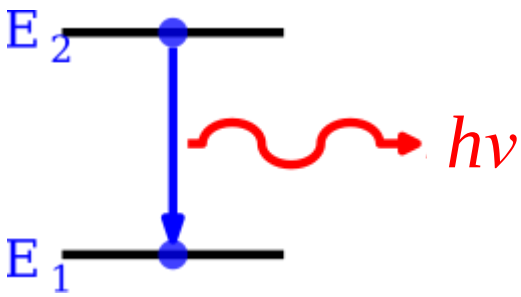

(2). Spontaneous Emission – the atom or molecule emits radiation independently of whether it is being irradiated at the wavelength of the transition or not. This process will occur in the dark. The rate is independent of the intensity of radiation at the wavelength of the transition (if any is present), and the emitted photons have random directions of propagation and random polarization.

Rate of spontaneous emission per molecule = $A_{2\rightarrow1}$

$A_{2\rightarrow1}$ has units of s^{-1}.

Einstein A and B coefficients

A side note: If we only need to worry about an excited state decaying by spontaneous emission, it is easy to figure out its lifetime.

For an initially excited population of $N_2(0)$, the population at a later time, $N_2(t)$, is governed by:

$$\frac{dN_2}{dt} = -N_2 A_{2\to1}$$

This gives

$$\frac{dN_2}{N_2} = -A_{2\to1}dt$$

This integrates to give:

$$N_2(t) = N_2(0)e^{-A_{2\to1}t}$$

The population in the excited state decays exponentially, just like any first-order kinetics process.

Rewriting this as $\frac{N_2(t)}{N_2(0)} = e^{-A_{2\to1}t} = e^{-t/\tau}$, the exponential decay time τ is just $1/A_{2\to1}$. (This assumes there are no other decay mechanisms possible.)

Einstein A and B coefficients

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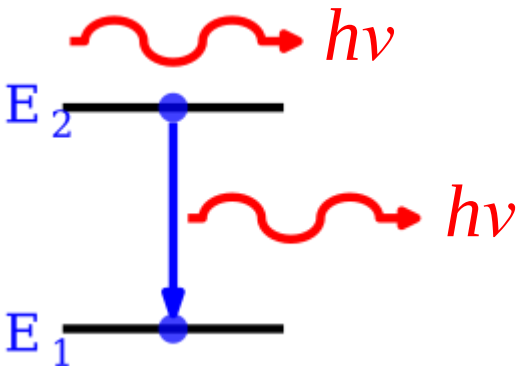

(3). Stimulated emission – the atom or molecule is stimulated to emit radiation by the radiation passing by. The emitted photon is identical to the photon that caused the emission. It has the same wavelength, energy, direction of propagation, polarization, phase, etc. The rate is proportional to the intensity of the radiation at the wavelength of the transition.

Rate of stimulated emission per molecule = $B_{2\rightarrow1}I(\omega_{21})$

$B_{2\rightarrow1}I(\omega_{21})$ has units of s^{-1}.

Now think about a simple absorption experiment:

Is the transmitted light intensity (I) larger or smaller than the incident light intensity (I_0)?

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In an ordinary absorption spectrometer, some of the light is absorbed, so I is smaller than I_0 (Maybe they're equal if no light is absorbed.)

In analytical chemistry, this gives the Beer-Lambert Law:

$$\frac{I_0}{I} = 10^{-\varepsilon \ell c}$$

Where c is the concentration (mol/L), ℓ is the length of the cell (cm), and ε is the molar extinction coefficient (L/(mol-cm)).

Now think about a simple absorption experiment:

But it isn't always true that $I < I_0$!

Under the right conditions, the incident light intensity can be amplified, instead of attenuated!

Now think about a simple absorption experiment:

The net rate of molecules being excited (and photons being absorbed) is $N_1 B_{2\leftarrow 1} I(\omega_{21})$.

Intensity of light

Einstein B coefficient

The net rate of molecules being stimulated to emit (and photons adding to the intensity of the transmitted light) is $N_2 B_{2\rightarrow 1} I(\omega_{21})$

Number of Molecules in the upper state that can be stimulated to emit

Intensity of light

Einstein B coefficient

The net rate of photons being added to the beam is

$N_2 B_{2\rightarrow 1} I(\omega_{21}) - N_1 B_{2\leftarrow 1} I(\omega_{21})$.

But $B_{2\rightarrow 1} = B_{2\leftarrow 1}$, so the net rate of photons being added to the beam is:

Rate of photon addition = $(N_2 - N_1)\, B_{21}\, I(\omega_{21})$

Light Amplification by Stimulated Emission of Radiation (Laser):

Rate of photon addition to the beam = $(N_2 - N_1)\, B_{21}\, I(\omega_{21})$

The incident light intensity can be amplified, but *only* if the number of molecules in the upper state (N_2) exceeds the number in the lower state (N_1). This is called a population inversion, and it is hard to achieve.

A population inversion cannot be achieved if a sample is in thermal equilibrium, because Boltzmann tells us that the ratio of the population of molecules in the upper state (N_2) to the lower state (N_1) is given by:

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT}.$$

But because $E_2 > E_1$, the exponent is negative and $\frac{N_2}{N_1} < 1$, so $N_2 < N_1$.

How can you achieve a population inversion?

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Hit the molecules with a (metaphorical) hammer!

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Some tricks that are used to create a nonthermal distribution:

- Run an electrical discharge through the laser medium
- Use an intense light beam to create a large excited state population
- Use a highly exothermic chemical reaction to generate a population inversion

Example 1: The Helium-Neon Laser

This was one of the first lasers to go into widespread use, because it was the least expensive laser of its time. It was the laser originally used in bar code scanners at the supermarket.

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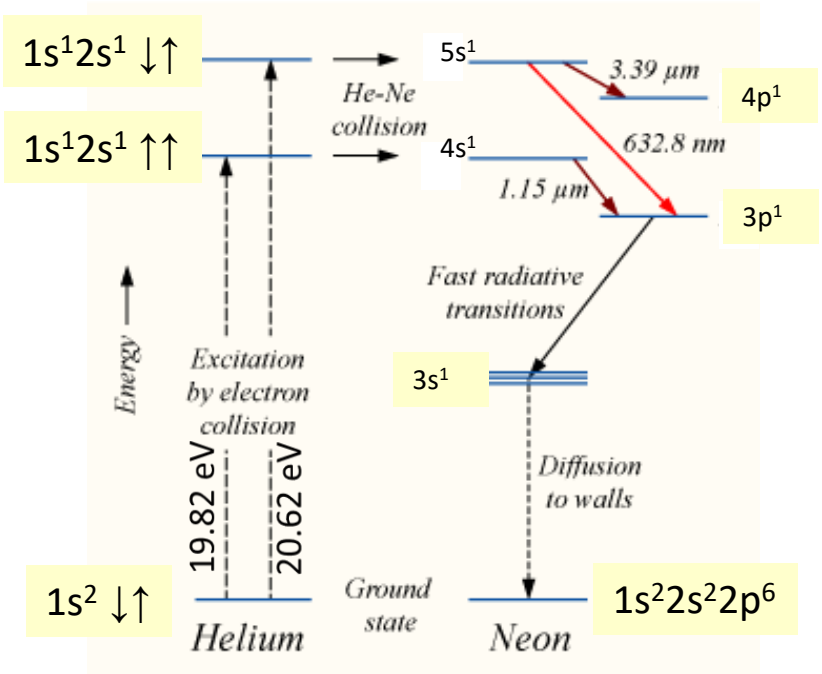
Helium is a unique gas in many ways. One unique feature is that its first excited configuration, $1s^1 2s^1$, lies higher in energy that the first excited state of any other neutral atom or molecule. This makes it useful for transferring large amounts of energy to other atoms or molecules.

Example 1: The Helium-Neon Laser

The process begins with an electrical discharge that excites the helium atoms to the $1s^1 2s^1$ configuration, with 19.82 or 20.62 eV of energy. This is HUGE! (For comparison, the strongest bond known, CO, has a bond energy of 11.11 eV.

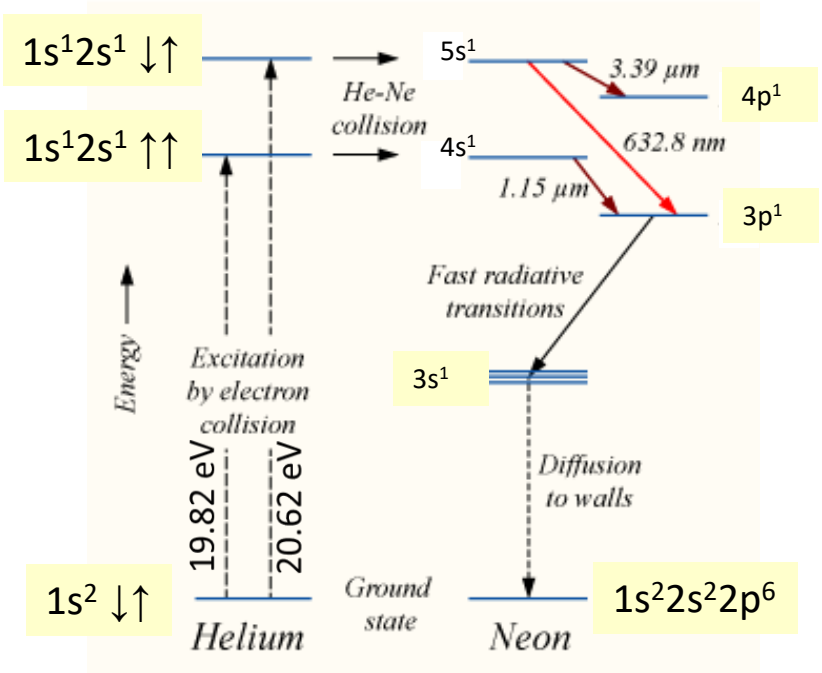
When He* collides with Ne, it excites one of the 2p electrons to the 5s orbital and drops its own 2s electron to the 1s orbital. This process occurs with high efficiency because the energy of the $1s^1 2s^1$ state of helium nearly matches the energy of the $1s^2 2s^2 2p^5 5s^1$ (abbreviated to $5s^1$) state of neon. This is called resonant energy transfer.



Example 1: The Helium-Neon Laser

The *selective* population of the $5s^1$ state of neon, without populating the lower-lying $3p^1$ state, means that a population inversion is created between these two states. This is exactly what is needed for laser action (light amplification by stimulated emission of radiation). Laser action between these two levels produces red light at 632.8 nm.

Population inversions also exist between the $5s^1$ and $4p^1$ levels, which can produce infrared light at 3.39 μm; also between the $4s^1$ and $3p^1$ levels, producing infrared light at 1.15 μm. Commercially produced helium-neon lasers (HeNe lasers) are optimized for production of 632.8 nm light, however.



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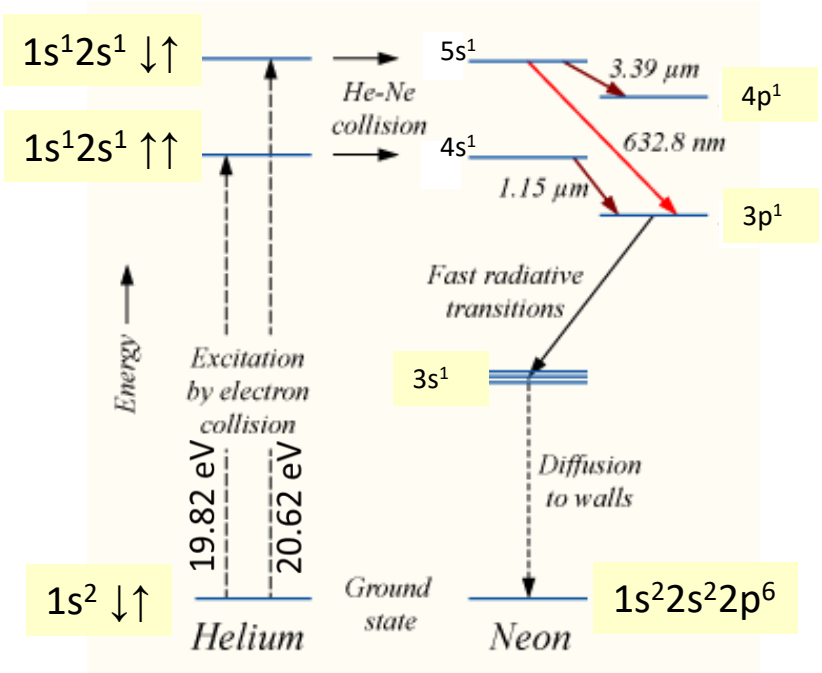

BUT THERE'S A PROBLEM!

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Here's the problem: We're not sending any photons into the system, so how can we have light amplification by stimulated emission of radiation (laser action)? Multiplying zero photons by any factor you like still gives you zero photons!

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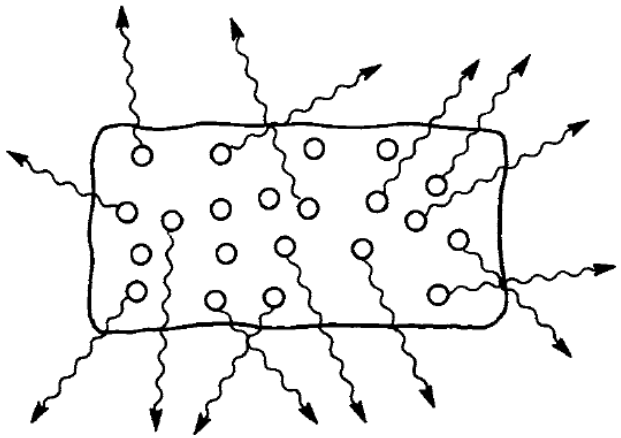

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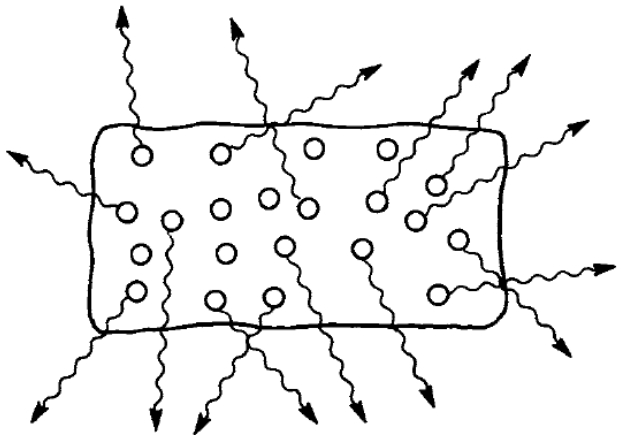
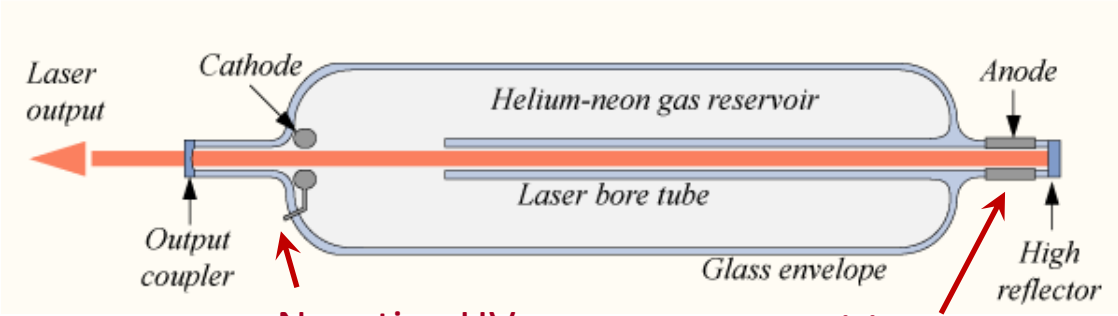


Some of the spontaneously emitted photons are going in the right direction to get out of the laser, and they can be amplified by stimulated emission. If they make it out of the exit window, we'll have a light source, but it won't be very well collimated. The solution is to put mirrors in, reflect the light that's going in the right direction back and forth, and amplify it!

Example 1: The Helium-Neon Laser

The problem is that when you construct the actual laser, the amplification per pass (by stimulated emission of radiation) is only about 1%! If you send in 100 photons, you only get 101 photons out.

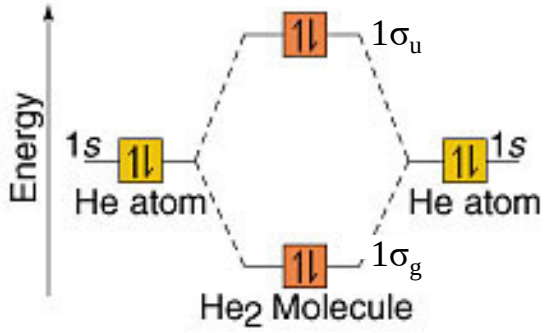


The solution is to put the lasing material in a laser cavity or oscillator, so that the laser light can bounce back and forth being amplified many times! If the gain per pass is only about 1%, you really can't afford very large losses per pass, so you need really excellent mirrors. In practice, the high reflector is as close to 100% reflective as you can get, and the output coupler is about 99% reflective, so you get about 1% losses (through output) every 2 passes (every roundtrip). These are not the kind of mirrors you have in your bathroom, which are about 90% reflective (at best)!

Spontaneous emission that happens to be directed along the optical axis stimulates more emission, while spontaneous emission going in other directions is lost. Because the light bounces back and forth ~100 times before escaping, the light must be traveling in exactly the right direction not to be lost. The beam is very well collimated.

Example 2: Excimer Lasers

Rare gas atoms don't form chemically bound dimers (Rg_2) because they put equal numbers of electrons in bonding orbitals and antibonding orbitals, and antibonding orbitals are more antibonding than bonding orbitals are bonding. For example, He_2:



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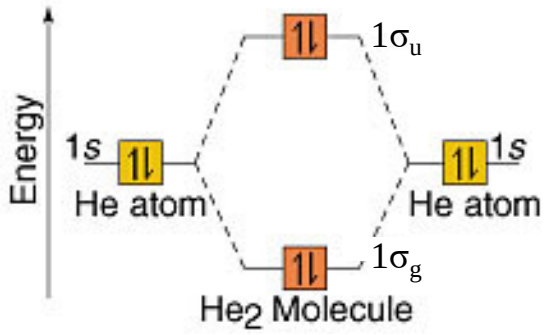

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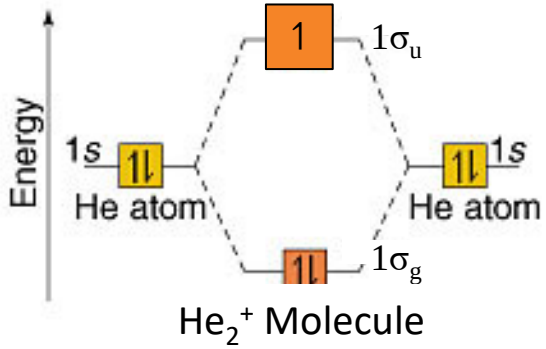
But if you remove an electron from the antibonding orbital, He_2^+ is reasonably strongly bound!



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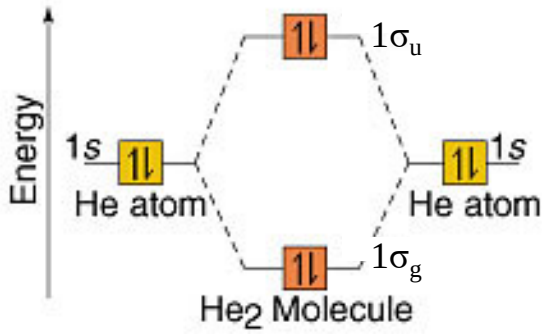

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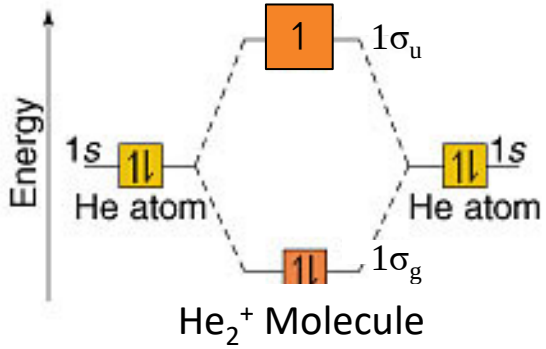

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Many molecules (like He_2) are very weakly bound (if at all) in the ground state but strongly bound in electronically excited states. These are called excimers, short for excited-state dimers.

Rare Gas Halide Lasers

Since the two atoms in a rare gas halide (like ArF, KrF, KrCl, etc.) are different, these should really be called **exciplex** lasers (for excited state complex). Most people call them excimer lasers, however. They share the characteristic that the system is unbound (or only very weakly bound) in the ground state but is strongly bound in the excited state.

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In these lasers, an electrical discharge excites the rare gas (Ar, Kr, or Xe) to an excited state in which one of the outer p electrons is placed in a higher orbital:

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But Kr $[\ldots]4s^2 4p^5 5s^1$ has one electron outside of the n=4 shell, just like ground state Rb $[\ldots]\ 4s^2 4p^6 5s^1$. In fact, the ionization energies of the two systems are nearly the same, and this is true for the first excited states of the other rare gases:

IE(Ar, $3s^2 3p^5 4s^1$) = 4.211 eV IE(K $3s^2 3p^6 4s^1$) = 4.341 eV

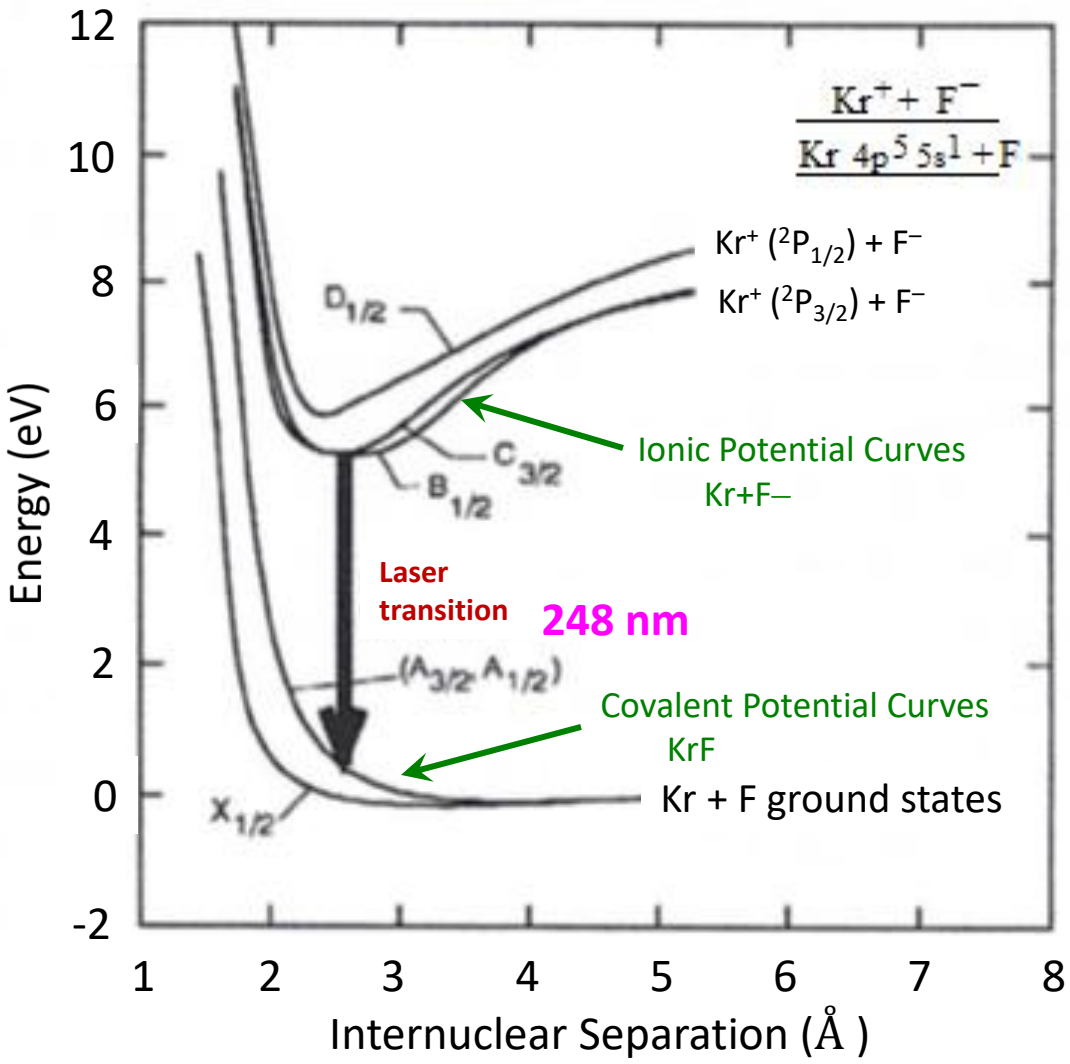
IE(Kr, $4s^2 4p^5 5s^1$) = 4.084 eV IE(Rb, $4s^2 4p^6 5s^1$) = 4.177 eV

IE(Xe, $5s^2 5p^5 6s^1$) = 3.814 eV IE(Cs, $5s^2 5p^6 6s^1$) = 3.894 eV

What happens when an excited state of Kr collides with an F atom (or even with F_2)?

Just like Rb + F_2 !

Rare Gas Halide Lasers



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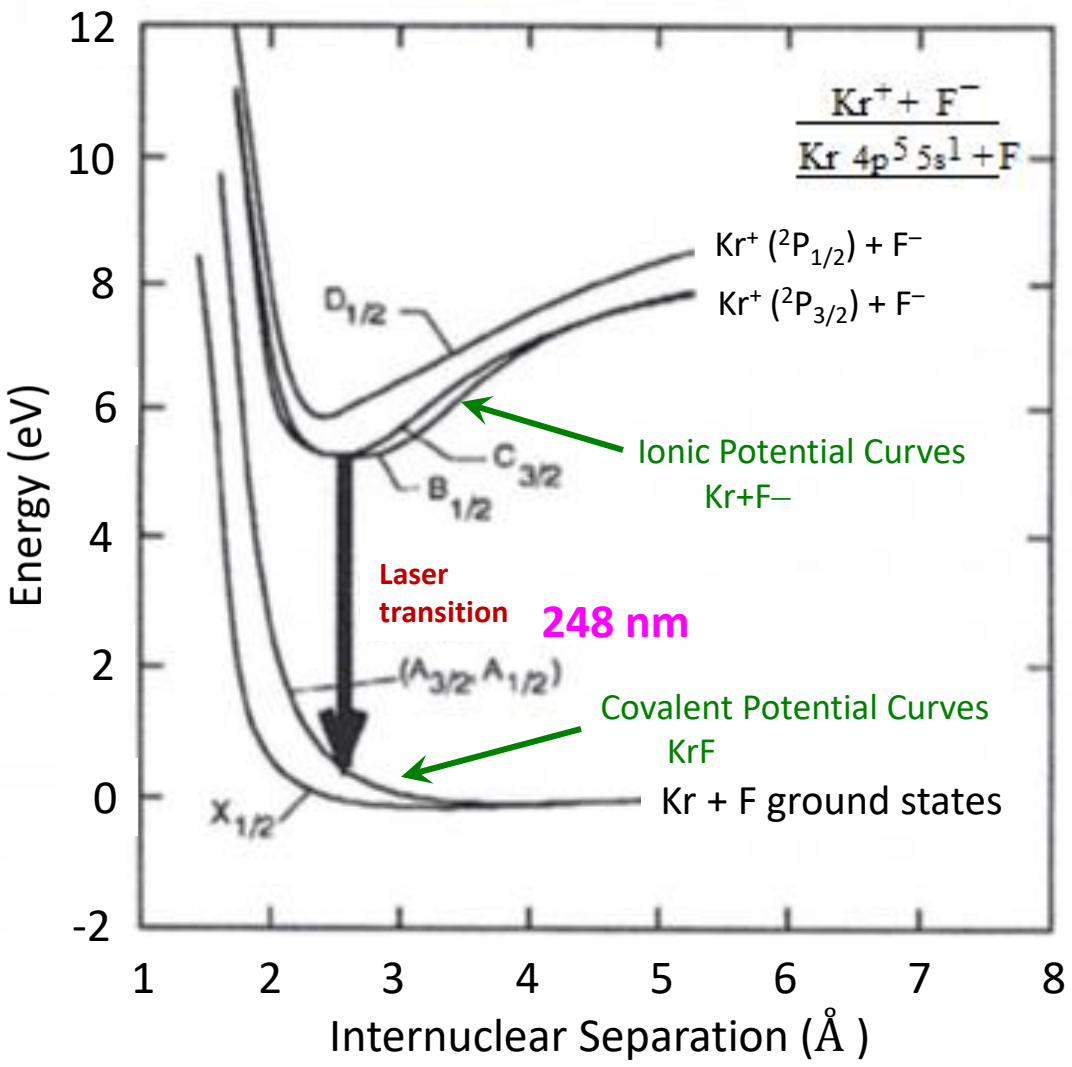


For many laser systems, the lasing process is self-terminating, because population builds up in the lower level, destroying the population inversion.

In this laser system that doesn't happen, because the lower level of the lasing transition dissociates. Population never builds up in it!

Estimating the laser photon energy:

To make the ion pair $Rg^+ + X^-$ from Rg + X requires an energy input of IE(Rg) – EA(X).

When the bound ionic molecule is formed, you get some of this energy back. This can be estimated as being equal to the bond energy of the corresponding alkali halide, $D_0(MX)$

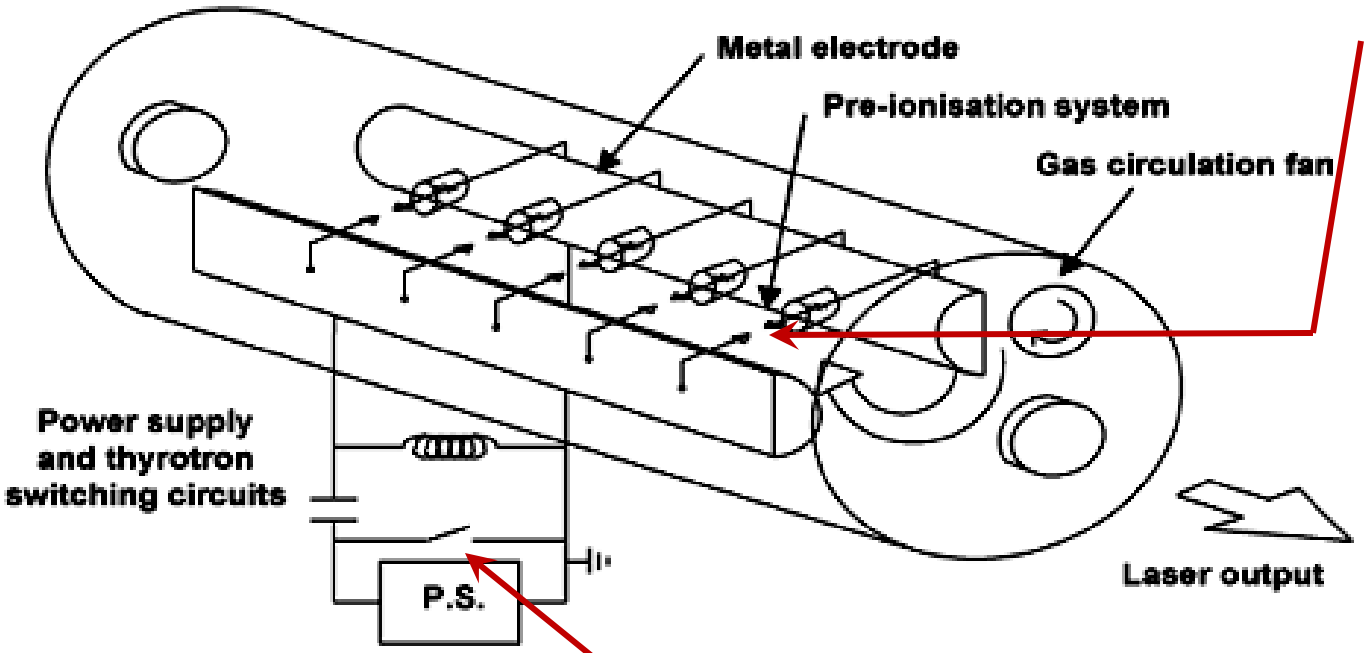
The remaining energy goes into the laser emission (hν) and the kinetic energy of the separating atoms, so $IE(Rg) - EA(X) - D_0(MX) = h\nu + KE(atoms)$

Thus, $h\nu = IE(Rg) - EA(X) - D_0(MX) - KE(atoms)$. If we ignore the KE of the atoms, we can get an estimate of the laser photon energy.

System	MX analog	IE(Rg)	EA(X)	$D_0(MX)$	hν(estimate)	hν(measured)
ArF	KF	15.755	3.399	5.07	7.29 eV	6.42 eV = 193 nm
KrCl	RbCl	13.996	3.615	4.34	6.04 eV	5.58 eV = 222 nm
KrF	RbF	13.996	3.399	5.00	5.60 eV	5.00 eV = 248 nm
XeCl	CsCl	12.127	3.615	4.58	3.93 eV	4.03 eV = 308 nm
XeF	CsF	12.127	3.399	5.15	3.58 eV	3.53 eV = 351 nm

Obviously, the separating atoms carry away a lot of energy in the lighter systems, especially ArF. But the approximation at least gives us a ballpark estimate of hν and more importantly, an understanding of the process.

How is it constructed?



Preionization is actually quite important. It is a discharge that occurs before the main discharge, emitting UV light. This light ionizes some species throughout the gas, making sure the main discharge fills the space between electrodes. No localized lightning bolts!

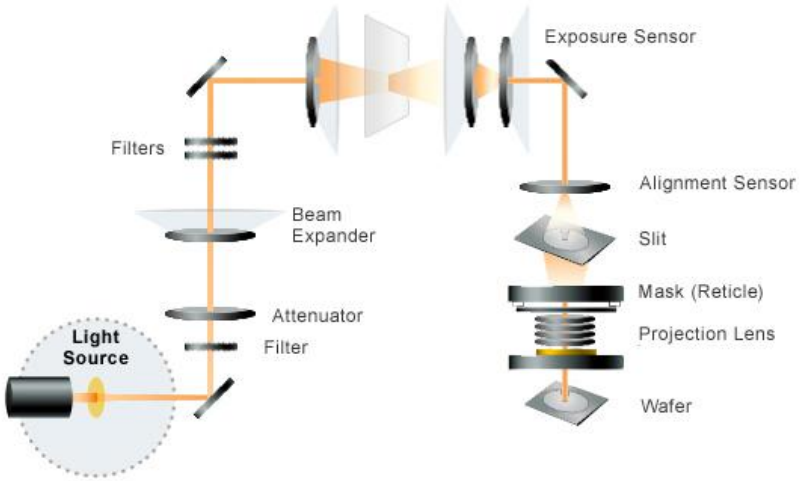
The gas mixture used for ArF (which emits 193 nm light) is 0.17% F_2, 6% Ar, 95% Ne, total pressure about 3 atm.

(Yes, these lasers actually use gaseous F_2 to generate UV light!)

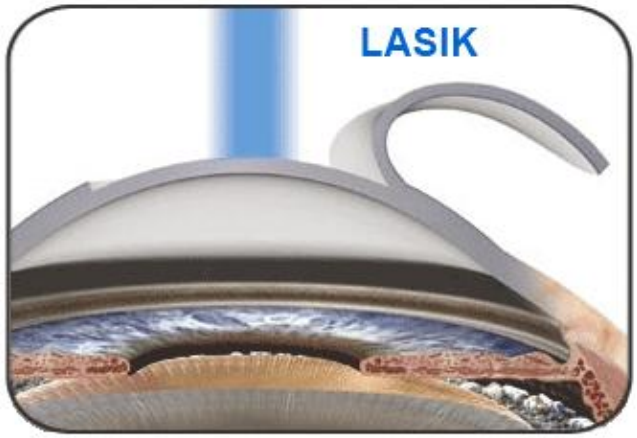
The switch here is actually pretty fancy. It uses an expensive component called a thyratron to switch 15-30 kV in about 10 ns. This fires a discharge across the preionization gaps, then a few ns later, between the main electrodes.

Main uses of Excimer Lasers

- Photolithography – Production of smaller and smaller circuits requires photolithography on tiny scales. Since the ability to form a small image is limited by the wavelength of the light, the ultraviolet wavelengths generated by excimer lasers are very useful in this regard. This is a BIG business.



- Laser radial keratotomy or LASIK eye surgery – Sculpting of the cornea so that its refractive power is matched to the lens, improving the focusing ability of the eye. This also is a BIG business. This is essentially controlled laser ablation of the cornea.



- Pump lasers for tunable dye lasers (XeCl laser, 308 nm).

Example 3. CO_2 Lasers

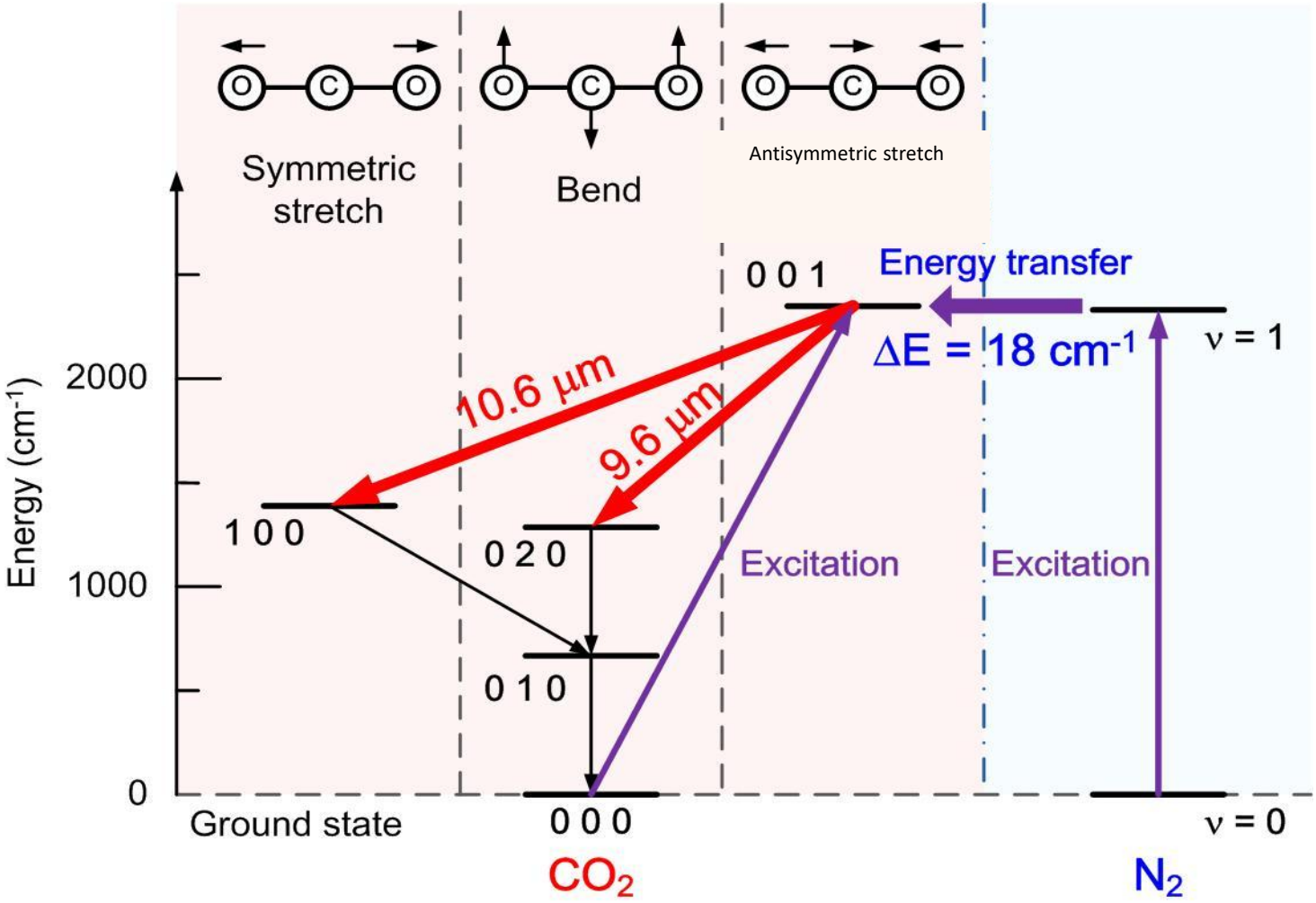
CO_2 lasers are the highest-power continuous wave (*i.e.*, not pulsed) lasers currently available, ranging from a few watts to about 100 kW (either is terrifying!). These are the lasers that are industrially used for precision cutting, welding, engraving, and marking of materials like metals and plastics. Also used in cosmetic surgery to remove fine lines and wrinkles, acne scars, hyperpigmentation, age spots, warts and moles, and certain skin cancers.

Example 3. CO_2 Lasers

CO_2 lasers typically use a gas mix of 10% CO_2, 12% N_2, and 78% He in an electrical discharge. Each component of the mixture has a well-defined purpose. It all begins when the electrical discharge excites N_2 to its first vibrational level. Because the N_2 (v=1) energy is an almost exact match with the energy of the antisymmetric stretch of CO_2, there is a very efficient energy transfer to excite one quantum of antisymmetric stretch in CO_2. This is another example of resonant energy transfer.

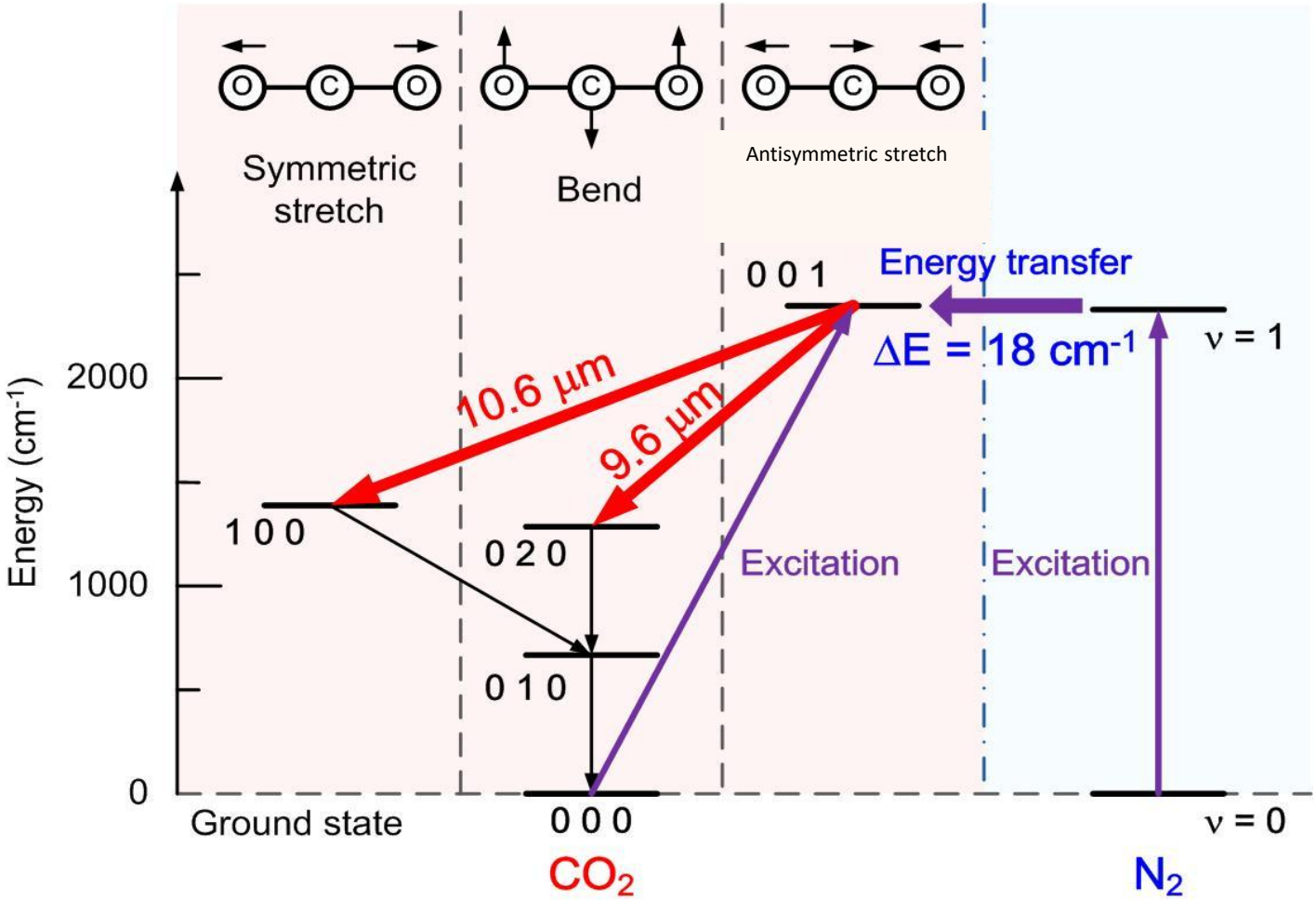
Example 3. CO_2 Lasers

The v=1 antisymmetric stretching level of CO_2 lies above the v=1 symmetric stretching level, which is not significantly populated at ordinary temperatures, so we have a population inversion and lasing at 10.6 μm(943 cm^{-1}) happens readily.



Example 3. CO_2 Lasers

To maintain the population inversion, the population in the lower level of the transition must be depleted quickly. Collisions with helium atoms are effective in dropping the CO_2 molecules in the v=1 symmetric stretching level to lower levels, allowing the population inversion to be maintained.



Relatively to other gas phase lasers, this is a highly efficient laser, converting 10-20% of the electrical power into laser energy.

Thanks for listening!

Anytime you'd like to ask me a question:

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