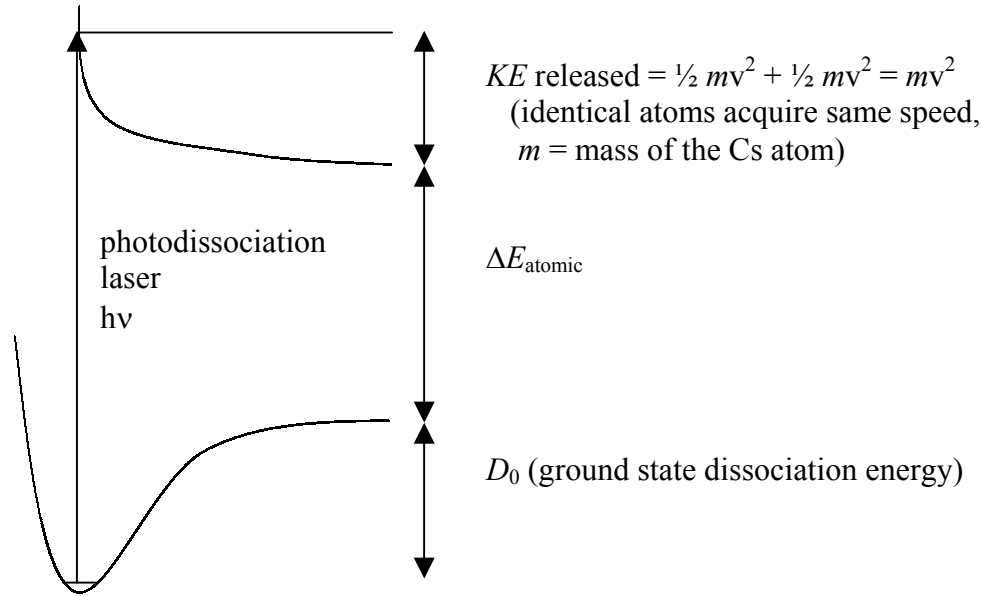


Absorption Lineshapes for Fast, Excited Atoms Created by Molecular Photodissociation

First approximation

First consider the ideal case of an initially stationary Cs_2 molecule in the ro-vibrational level $v = 0, J = 0$ that absorbs a photon and photodissociates to create one fast ground state atom and one fast atom in the $5D_{3/2}$ excited state.

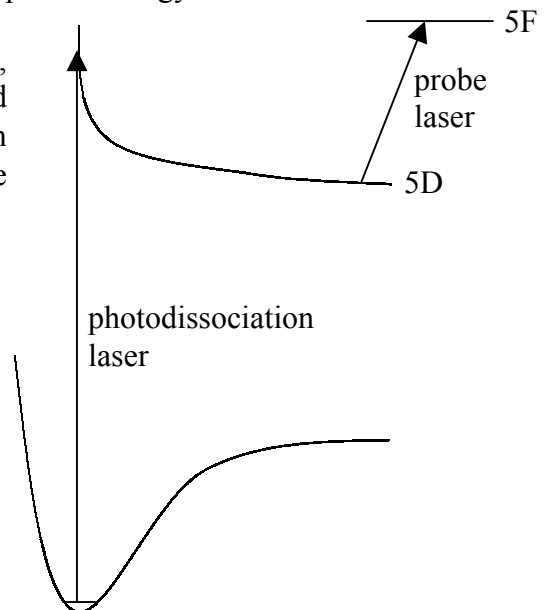


Thus $m v^2 = h\nu - \Delta E_{\text{atomic}} - D_0(\text{g.s.}) \Rightarrow$ all excited $5D_{3/2}$ atoms are produced with the same speed v_0 obtained by solving this equation for the specific photon energy.

If we neglect homogeneous broadening for now, then the probability that a probe laser photon tuned near the $5D_{3/2} \rightarrow 5F$ atomic transition (with detuning $\Delta\omega$) will be absorbed by an atom in the $5D_{3/2}$ state moving with velocity \vec{v} is

$$\delta(\Delta\omega - \vec{k}_L \cdot \vec{v}) = \delta\left(\Delta\omega - \frac{\omega_0 v}{c} \cos\theta\right).$$

The probability that the atom has velocity in the range $v_x \rightarrow v_x + dv_x, v_y \rightarrow v_y + dv_y, v_z \rightarrow v_z + dv_z$, is



$$f(\vec{v})d^3\vec{v}.$$

The spectrum will therefore be given by

$$I(\Delta\omega) \propto N \int \delta(\Delta\omega - \frac{\omega_0 v}{c} \cos\theta) f(\vec{v}) d^3\vec{v}$$

where N is the number of $5D_{3/2}$ atoms. In our case, we assume all atoms are produced with the same speed v_0 so

$$f(\vec{v})d^3\vec{v} = C\delta(v - v_0)d^3\vec{v}.$$

Normalization gives the value for C

$$1 = C \int \delta(v - v_0) v^2 dv d\Omega = 4\pi v_0^2 C \quad \Rightarrow \quad C = \frac{1}{4\pi v_0^2},$$

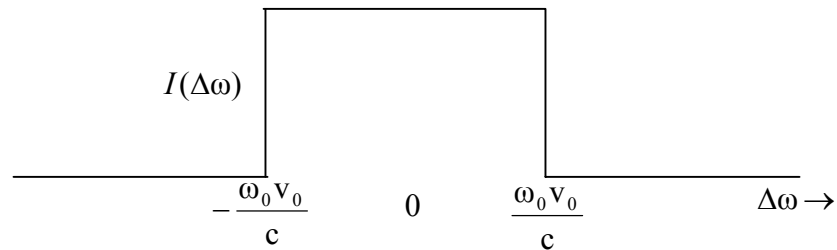
so

$$f(\vec{v})d^3\vec{v} = \frac{1}{4\pi v_0^2} \delta(v - v_0) d^3\vec{v}.$$

Therefore

$$\begin{aligned} I(\Delta\omega) &\propto N \int \delta(\Delta\omega - \frac{\omega_0 v}{c} \cos\theta) \frac{1}{4\pi v_0^2} \delta(v - v_0) v^2 dv d(\cos\theta) d\phi \\ &= \frac{N}{2} \int \delta(\Delta\omega - \frac{\omega_0 v_0}{c} \cos\theta) d(\cos\theta) \\ &= \frac{Nc}{2\omega_0 v_0} \int \delta(\frac{c\Delta\omega}{\omega_0 v_0} - \cos\theta) d(\cos\theta) \\ &= \begin{cases} \frac{Nc}{2\omega_0 v_0} & \text{if } -\frac{\omega_0 v_0}{c} < \Delta\omega < \frac{\omega_0 v_0}{c} \\ 0 & \text{otherwise.} \end{cases} \end{aligned}$$

This gives us the “square” lineshape



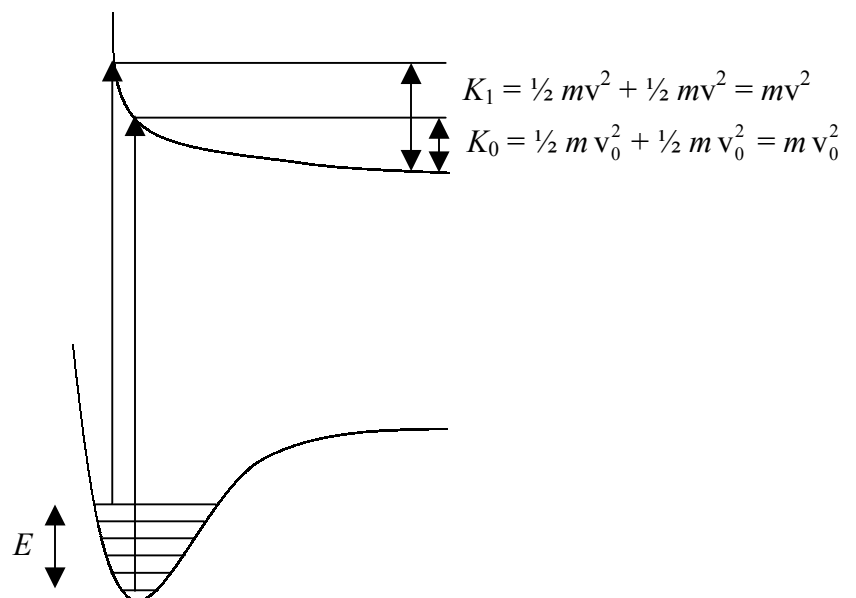
Thermal distribution of population in the v, J levels of the ground state

Now we consider the fact that not all molecules initially reside in the $v = 0, J = 0$ level of the ground state.

$5D_{3/2}$ atoms created through photodissociation of molecules initially populating the $v = 0, J = 0$ level will still acquire a speed $v_0 = \sqrt{K_0/m}$ where K_0 is the kinetic energy released. But excited atoms created through photodissociation of molecules in a higher ground state level (characterized by energy E relative to the $v = 0, J = 0$ level) will acquire a higher speed:

$$v(E) = \sqrt{\frac{K_0 + E}{m}}$$

$$\text{or } E = mv^2 - mv_0^2$$



Density of states argument

We assume that the population of ground state v , J levels follows a thermal distribution:

$$N(v, J) \propto (2J + 1) \exp[-(E_{vib} + E_{rot})/kT]$$

$$\propto (2J + 1) \exp[-(\omega_e(v + \frac{1}{2}) + B_e J(J + 1))/kT]$$

and we approximate the level energies by $E(v, J) = E_{vib} + E_{rot} = \omega_e(v + \frac{1}{2}) + B_e J(J + 1)$.

Since there are many thousands of thermally populated ground state ro-vibrational levels, we can treat the distribution as a continuum.

For $v = 0$, the number of rotational levels between E and $E + dE$ is given by:

$$g(E)dE = N(v = 0, J)dJ = N(v = 0, J) \frac{dJ}{dE} dE = \frac{N(v = 0, J)}{dE/dJ} dE$$

$$= \frac{(2J + 1) \exp\left[-\left(\frac{\omega_e}{2} + B_e J(J + 1)\right)/kT\right]}{(2J + 1)B_e} dE$$

$$= \frac{1}{B_e} \exp(-\omega_e/2kT) \exp[-B_e J(J + 1)/kT] dE$$

$$= \frac{\exp(-E/kT)}{B_e} dE$$

which is valid for $E > \frac{\omega_e}{2}$. For $E < \frac{\omega_e}{2}$, the density of states $g(E)dE = 0$.

Similarly, for $v = 1$, the number of levels with energy in the range E to $E + dE$ is given by

$$g(E)dE = N(v = 1, J)dJ = \frac{N(v = 1, J)}{dE/dJ} dE$$

$$= \frac{(2J + 1) \exp\left[-\left(\frac{3\omega_e}{2} + B_e J(J + 1)\right)/kT\right]}{(2J + 1)B_e} dE$$

$$= \frac{\exp(-E/kT)}{B_e} dE$$

for $E > \frac{3\omega_e}{2}$ and 0 otherwise.

Thus we see that each v makes the same contribution to the density of states, but that only those v 's with $\omega_e(v + \frac{1}{2}) < E$ contribute.

Therefore, the total number of levels in the range E to $E + dE$ is given by:

$$g(E)dE = \sum_{v=0}^{v_{\max}} \frac{\exp[-E/kT]}{B_e} dE = \frac{\exp[-E/kT]}{B_e} dE \sum_{v=0}^{v_{\max}} 1 = \frac{\exp[-E/kT]}{B_e} dE (v_{\max} + 1).$$

But $v_{\max} = \frac{E}{\omega_e} - \frac{1}{2}$ so $v_{\max} + 1 = \frac{E}{\omega_e} + \frac{1}{2} \approx \frac{E}{\omega_e}$ for $\frac{E}{\omega_e} \gg \frac{1}{2}$. Thus it is reasonable to take the density of states to be given by

$$g(E)dE = AE \exp[-E/kT] dE$$

where A is a constant given by $A = \frac{1}{\omega_e B_e}$.

Numerical simulations of the probability $g(E)dE$ of finding the ground state rovibrational energy between E and $E + dE$, based on the full set of vibration-rotation constants of the CS_2 molecule, show that this is a good approximation.

Back to the effect of the thermal distribution of population in the ground state v , J levels

The speed v of the fast excited atom created in the photodissociation process is directly related to the rovibrational energy E of the ground state molecule that was dissociated:

$$E = m(v^2 - v_0^2)$$

or

$$v^2 = \frac{E}{m} + v_0^2 .$$

The velocity distribution function is given by

$$f(\bar{v})d^3\bar{v} = 4\pi f(v)v^2 dv = g(E)dE ,$$

and

$$f(v) = \frac{g(E)dE}{4\pi v^2 dv} = \frac{Am(v^2 - v_0^2)}{4\pi v^2} \exp\left[-m(v^2 - v_0^2)/kT\right] \frac{dE}{dv} .$$

Thus we find

$$f(\bar{v})d^3\bar{v} = 4\pi f(v)v^2 dv = Am(v^2 - v_0^2) \exp\left[-m(v^2 - v_0^2)/kT\right] \frac{dE}{dv} dv .$$

Finally, since

$$\frac{dE}{dv} = 2mv ,$$

we can write

$$f(\bar{v})d^3\bar{v} = \begin{cases} 2Am^2(v^3 - vv_0^2) \exp\left[-m(v^2 - v_0^2)/kT\right] dv & \text{for } v > v_0 \\ 0 & \text{for } v < v_0 . \end{cases}$$

However, due to the fact that the Doppler shift depends on the direction of the velocity vector, rather than just on the magnitude, we must explicitly include the angular dependence:

$$f(\bar{v})d^3\bar{v} = \begin{cases} \frac{2}{4\pi} Am^2(v^3 - vv_0^2) \exp\left[-m(v^2 - v_0^2)/kT\right] dv d(\cos\theta) d\phi & \text{for } v > v_0 \\ 0 & \text{for } v < v_0 . \end{cases}$$

Finally, the absorption lineshape is given by

$$\begin{aligned} I(\Delta\omega) &= (const.) \int \delta\left(\Delta\omega - \frac{\omega_0 v}{c} \cos\theta\right) f(\bar{v}) d^3\bar{v} \\ &= (const.) \int_{v_0}^{\infty} (v^3 - vv_0^2) \exp\left[-m(v^2 - v_0^2)/kT\right] dv \int_{-1}^1 \delta\left(\Delta\omega - \frac{\omega_0 v}{c} \cos\theta\right) d(\cos\theta) \end{aligned}$$

$$\begin{aligned}
&= (const.) \int_{v_0}^{\infty} (v^3 - vv_0^2) \exp[-m(v^2 - v_0^2)/kT] dv \int_{-1}^1 \frac{c}{\omega_0 v} \delta\left(\frac{c\Delta\omega}{\omega_0 v} - \cos\theta\right) d(\cos\theta) \\
I(\Delta\omega) &= (const.) \int_{v_0}^{\infty} \left\{ \begin{array}{l} (v^3 - vv_0^2) \exp[-m(v^2 - v_0^2)/kT] dv \quad \text{for } -\frac{\omega_0 v}{c} < \Delta\omega < \frac{\omega_0 v}{c} \\ 0 \quad \text{otherwise} \end{array} \right\}.
\end{aligned}$$

Effect of the initial thermal distribution of molecular velocities

Next we consider the effect of the initial thermal distribution of molecular center of mass velocities (within each v , J level). We assume that the velocity of the center of mass is unchanged in the photodissociation process. However, this center of mass velocity simply adds to the excited atom velocity created through the photodissociation process (i.e. the excited atom velocity in the lab frame, \bar{v}_{lab} , is equal to the velocity \bar{v} of the excited atom in the center of mass frame, plus the center of mass velocity \bar{v}_{CM} : $\bar{v}_{lab} = \bar{v} + \bar{v}_{CM}$).

We label the center of mass velocity with a prime ($\bar{v}_{CM} \equiv \bar{v}'$) and we note that \bar{v}' is completely independent of \bar{v} , which is the velocity of the excited atom in the center of mass frame (i.e. the velocity “created” in the photodissociation process).

We can write the $5D_{3/2} \rightarrow 5F$ absorption coefficient for a fast $5D_{3/2}$ atom created from photodissociation of a molecule with center of mass velocity component v'_z as:

$$I(\Delta\omega, v'_z) = (const.) \int \delta\left(\Delta\omega - \frac{\omega_0 v'_z}{c} - \frac{\omega_0 v}{c} \cos\theta\right) f(\bar{v}) d^3\bar{v}$$

since the z component of center of mass velocity and the z component of the velocity in the CM frame (created in the photodissociation process) simply add to give the total z component of velocity in the laboratory frame. Therefore

$$\begin{aligned}
I(\Delta\omega, v'_z) &= (\text{const.}) \int_{v_0}^{\infty} (v^3 - vv_0^2) \exp[-m(v^2 - v_0^2)/kT] dv \int_{-1}^1 \delta\left(\Delta\omega - \frac{\omega_0 v'_z}{c} - \frac{\omega_0 v}{c} \cos\theta\right) d(\cos\theta) \\
&= (\text{const.}) \int_{v_0}^{\infty} (v^3 - vv_0^2) \exp[-m(v^2 - v_0^2)/kT] dv \int_{-1}^1 \frac{c}{\omega_0 v} \delta\left(\frac{c}{\omega_0 v} (\Delta\omega - \frac{\omega_0 v'_z}{c}) - \cos\theta\right) d(\cos\theta) \\
I(\Delta\omega, v'_z) &= (\text{const.}) \int_{v_0}^{\infty} \begin{cases} (v^2 - v_0^2) \exp[-m(v^2 - v_0^2)/kT] dv & \text{for } -\frac{\omega_0 v}{c} < (\Delta\omega - \frac{\omega_0 v'_z}{c}) < \frac{\omega_0 v}{c} \\ 0 & \text{otherwise} \end{cases}
\end{aligned}$$

Next we average over the initial thermal distribution of center of mass z component of molecular velocity:

$$\begin{aligned}
I(\Delta\omega) &= (\text{const.}) \int_{-\infty}^{\infty} P(v'_z) dv'_z \\
&= (\text{const.}) \int_{v_0}^{\infty} \begin{cases} (v^2 - v_0^2) \exp[-m(v^2 - v_0^2)/kT] dv & \text{for } -\frac{\omega_0 v}{c} < (\Delta\omega - \frac{\omega_0 v'_z}{c}) < \frac{\omega_0 v}{c} \\ 0 & \text{otherwise} \end{cases}
\end{aligned}$$

Note that v'_z and v are independent variables!

According to A. Corney, "Atomic and Laser Spectroscopy", Clarendon Press, Oxford, 1977 (p248), the thermal distribution of center of mass z component of molecular velocity is

$$P(v'_z) = \left(\frac{M}{2\pi kT}\right)^{1/2} \exp\left[-\frac{M(v'_z)^2}{2kT}\right]$$

where M is the molecular mass and $M = 2m$ (m is the atomic mass used above).

Thus we have

$$I(\Delta\omega) = (\text{const.}) \int_{-\infty}^{\infty} \left(\frac{M}{2\pi kT} \right)^{1/2} \exp\left[-\frac{M(v'_z)^2}{2kT} \right] dv'_z$$

$$\int_{v_0}^{\infty} \left\{ \begin{array}{ll} (v^2 - v_0^2) \exp\left[-m(v^2 - v_0^2)/kT \right] dv & \text{for } -\frac{\omega_0 v}{c} < (\Delta\omega - \frac{\omega_0 v'_z}{c}) < \frac{\omega_0 v}{c} \\ 0 & \text{otherwise} \end{array} \right.$$

Homogeneous broadening

Finally, we must include homogeneous broadening by convoluting the lineshape above with a Lorentzian function ($\Gamma = \text{fwhm}$ of the Lorentzian function describing natural broadening, pressure broadening, and power broadening/optical pumping effects).

$$I(\Delta\omega) = (\text{const.}) \int_{-\infty}^{\infty} \frac{\Gamma/2\pi}{(\omega - \omega')^2 + (\Gamma/2)^2} d\omega' \int_{-\infty}^{\infty} \left(\frac{M}{2\pi kT} \right)^{1/2} \exp\left[-\frac{M(v'_z)^2}{2kT} \right] dv'_z$$

$$\int_{v_0}^{\infty} \left\{ \begin{array}{ll} (v^2 - v_0^2) \exp\left[-m(v^2 - v_0^2)/kT \right] dv & \text{for } -\frac{\omega_0 v}{c} < (\Delta\omega' - \frac{\omega_0 v'_z}{c}) < \frac{\omega_0 v}{c} \\ 0 & \text{otherwise} \end{array} \right.$$

where we note that $\Delta\omega \equiv \omega - \omega_0$ is the laser detuning from the $5D_{3/2} \rightarrow 5F$ resonance frequency ω_0 , and $\Delta\omega' \equiv \omega' - \omega_0$.

Hyperfine structure

Lastly, we must include the effect of the four $5D_{3/2}$ state hyperfine levels ($F = 2, 3, 4, 5$) by calculating the absorption lineshape four times and adding them together with appropriate weighting ($2F + 1$) and offsets (slightly different ω_0 values). The upper 5F state hyperfine splittings are sufficiently small that they can be neglected.