Rotation states of diatomic molecules – Simplest case.

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The rotational energy are easily calculated. We can think of the molecules as a dumbdell, which can rotate about its center of mass. The classical energy of rotation is

$$E_{rot} = \frac{1}{2} I \omega^2$$

where I is the moment of inertia and ω is the angular velocity. Since the angular momentum L is

$$L = I\omega$$

It follows that $\omega = \frac{L}{I}$ and the rotation energy is

$$E_{rot} = \frac{1}{2I} L^2$$

This formula is also valid in quantum mechanics, if we use the correct quantized values

$$L^2 \to \hbar^2 l(l+1)$$

for L^2. Hence the rotation energy of diatomic molecule is

$$E_{rot}(l) = \frac{1}{2I} \hbar^2 l(l+1)$$

14.6 A simple model for the rotational energy is

$$\varepsilon_{lm} = \frac{\hbar^2}{2I} l(l+1)$$

where $l = 0, 1, 2, \ldots,$ $m = -\ell, \ldots, l$, and I is the moment of inertia. Thus

$$Z_{rot} = \sum_{l=0}^{\infty} (2l+1)\exp[-\frac{\beta\hbar^2 l(l+1)}{2I}]$$

(b) For $k_B T >> \hbar^2/(2I)$ approximate the sum over *l* by an integral. Show that

$$\frac{C_{rot}}{k_B} \approx 1$$

How about the entropy vs temperature?

(c) Make a quantitative sketch of U/N and C_{rot} as functions of temperature. Does C_{rot} approach the asymptotic value from above or below?

((**Solution**))

We consider the quantum state given by $|l,m\rangle$, where

$$\hat{\boldsymbol{L}}^2|l,m\rangle = \hbar^2 l(l+1)^2|l,m\rangle, \qquad \hat{L}_z|l,m\rangle = \hbar^2 l(l+1)^2|l,m\rangle$$

where *m* = -*l*, -*l*+1,…, *l*-1, and *l* (2*l*+1, fold)

The partition function for the canonical ensemble

$$\begin{aligned} Z_C &= \sum_{l=0}^{\infty} (2l+1)\exp[-\beta\varepsilon(l)] \\ &= \sum_{l=0}^{\infty} (2l+1)\exp[-\beta\frac{\hbar^2 l(l+1)}{2I}] \end{aligned}$$

where the energy eigenvalue for the state $|l,m\rangle$ is given by

$$\varepsilon(l) = \frac{\hbar^2 l(l+1)}{2I}.$$

We define the characteristic temperature as

$$\Theta = \frac{\hbar^2}{2k_B I}.$$

$$Z_C = \sum_{l=0}^{\infty}(2l+1)\exp[-\frac{\Theta}{T}l(l+1)]$$

The Helmholtz free energy

$$F = -k_B T \ln Z_C$$

The internal energy:

$$E = -\frac{\partial \ln Z_C}{\partial \beta} = k_B T^2 \frac{\partial \ln Z_C}{\partial T}$$

The heat capacity:

$$C = \frac{\partial E}{\partial T}$$

The entropy S is

$$S = k_B(\ln Z_C - \beta\frac{\partial}{\partial \beta}\ln Z_C) .$$

$$\begin{aligned} S &= \frac{E}{T} + k_B \ln Z_C \\ &= k_B \ln Z_C + k_B T\frac{\partial \ln Z_C}{\partial T} \\ &= k_B(\ln Z_C - \beta\frac{\partial \ln Z_C}{\partial \beta} \end{aligned}$$

(a) The low temperature limit ($T << \Theta$)

$$Z_C \approx 1 + 3e^{-2\Theta/T}$$

$$E = k_B T^2 \frac{\partial \ln Z_C}{\partial T} = k_B T^2 \frac{1}{Z_C}\frac{\partial Z_C}{\partial T} = 6k_B\Theta\frac{e^{-2\Theta/T}}{1+3e^{-2\Theta/T}} \approx 6k_B\Theta e^{-2\Theta/T}$$

$$C = \frac{dE}{dT} = 12k_B \frac{\Theta^2}{T^2} e^{-2\Theta/T}$$

(b) The high temperature limit ($T >> \Theta$)

$$Z_C \approx \int_0^\infty dx(2x+1)\exp[-\frac{\Theta}{T}x(x+1)] = \frac{T}{\Theta}$$

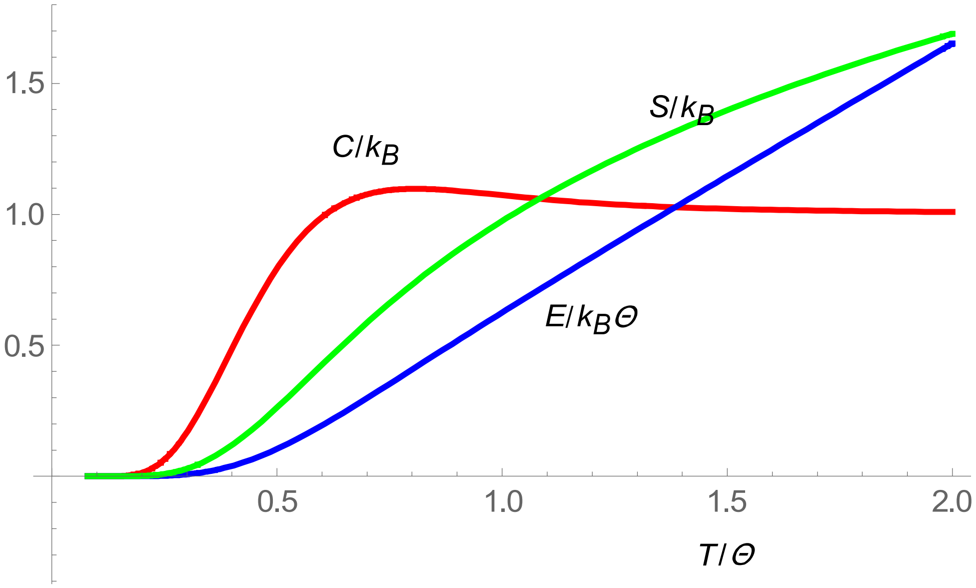
$$E = k_B T^2 \frac{\partial \ln Z_C}{\partial T} = k_B T$$

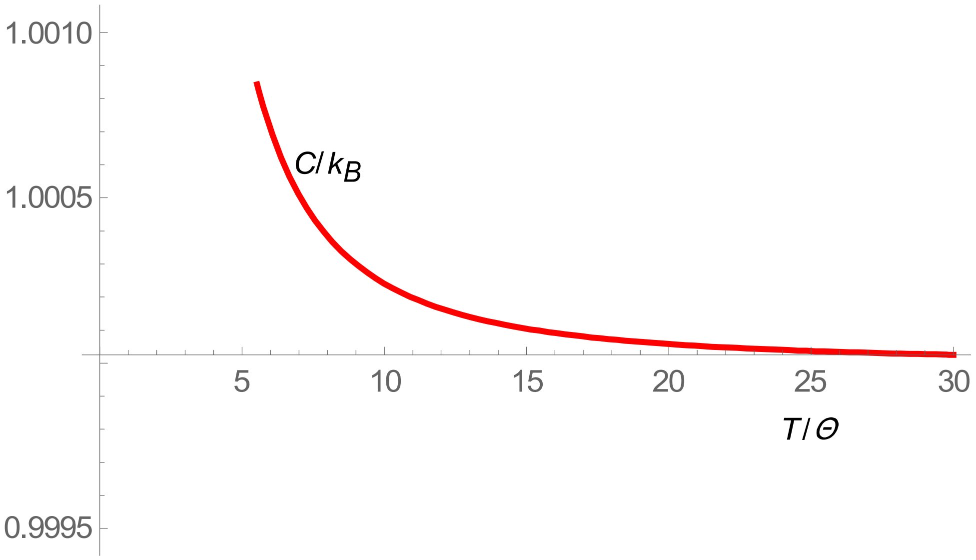
$$C = k_B$$

$$S = k_B[\ln\left(\frac{T}{\Theta}\right) + 1]$$

(c)

We make a plot of $\frac{E}{k_B\Theta}$, $\frac{C}{k_B}$ and $\frac{S}{k_B}$ as a function of a reduced temperature $\frac{T}{\Theta}$.




1.0010
1.0005
0.9995
C/k_B
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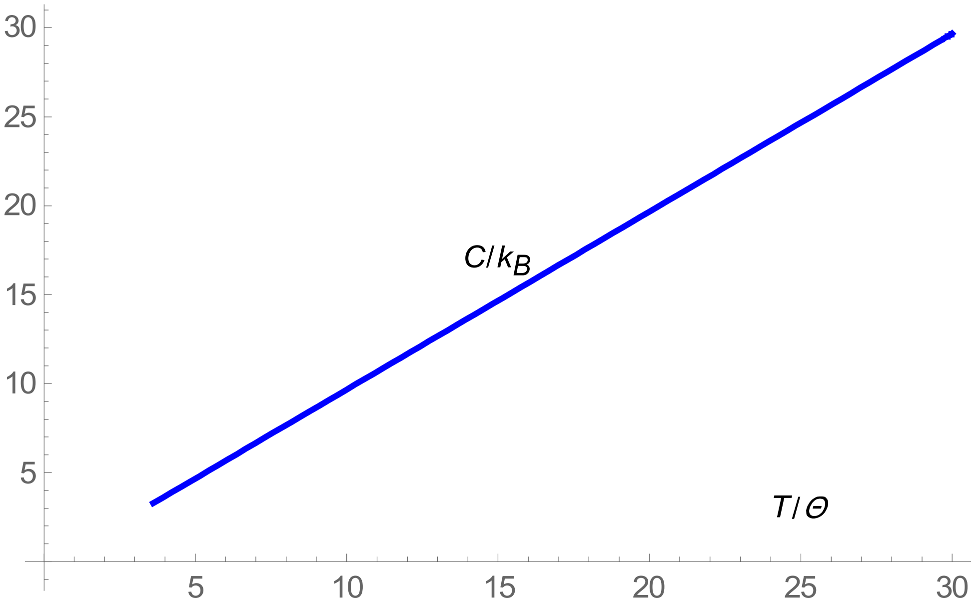
30
T/Θ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C/k_B
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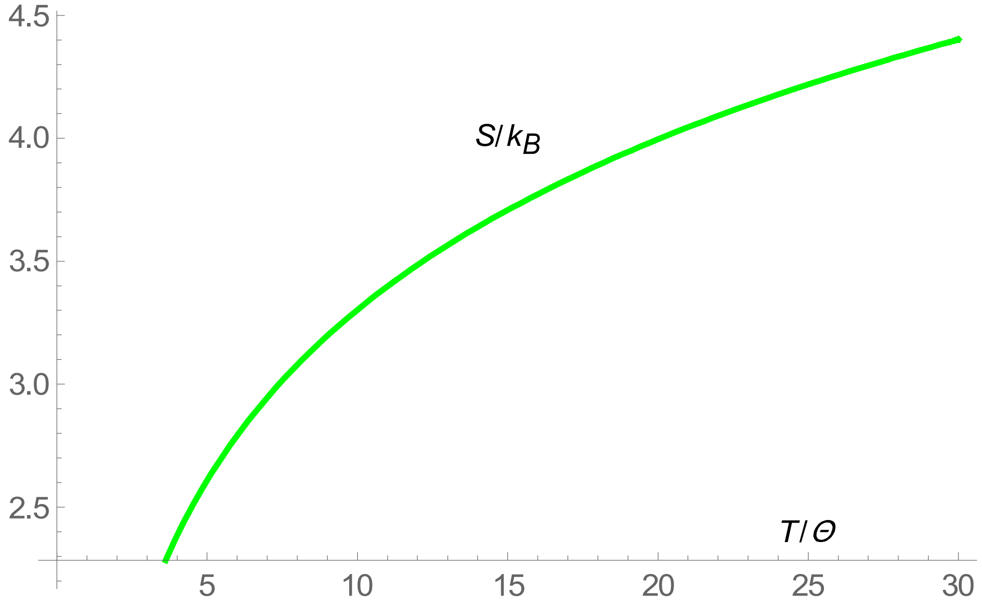


((**Mathematica**))

```
Clear["Global`*"];
f[x_, n_] := (2 n + 1) Exp[-1/x n (n + 1)];
N1 = 7;
ZC = Sum[f[T/θ, n], {n, 0, N1}] // Simplify;
E1 = kB T^2 D[Log[ZC], T] // Simplify;
C1 = D[E1, T] // Simplify;
S1 = kB (Log[ZC] + T D[Log[ZC], T]) // Simplify;
Ey1 = E1/(kB θ) /. {T → θ x};
Cy1 = C1/kB /. {T → θ x};
Sy1 = S1/kB /. {T → θ x};
p1 = Plot[Evaluate[Cy1], {x, 0, 2},
   PlotPoints → 100, PlotStyle → {Red, Thick}];
p2 = Plot[Evaluate[Ey1], {x, 0, 2},
   PlotPoints → 100, PlotStyle → {Blue, Thick}];
p3 = Plot[Evaluate[Sy1], {x, 0, 2},
   PlotPoints → 100, PlotStyle → {Green, Thick}];
p4 =
  Graphics[
   {Text[Style["T/Θ", Italic, Black, 10],
     {1.5, -0.3}],
    Text[Style["C/k_B", Italic, Black, 10],
     {0.7, 1.25}],
    Text[Style["E/k_BΘ", Italic, Black, 10],
     {1.2, 0.6}],
    Text[Style["S/k_B", Italic, Black, 10],
     {1.4, 1.4}]}];
Show[p1, p2, p3, p4, PlotRange → All]
```

((**Huang**))

8.6

(a)

$$\begin{aligned}\ln Q_{\text{rot}} &\approx \ln\left(1+\exp\left(-\beta\hbar^2/I\right)\right) \approx \exp\left(-\beta\hbar^2/I\right)\\ \frac{U}{N} &= -\frac{\partial \ln Q_{\text{rot}}}{\partial\beta} = \frac{\hbar^2}{I}\exp\left(-\frac{\beta\hbar^2}{I}\right)\end{aligned}$$

$$\frac{c_{\text{rot}}}{k} \approx 3\left(\frac{\beta\hbar^2}{I}\right)^2 \exp\left(-\frac{\beta\hbar^2}{I}\right)$$

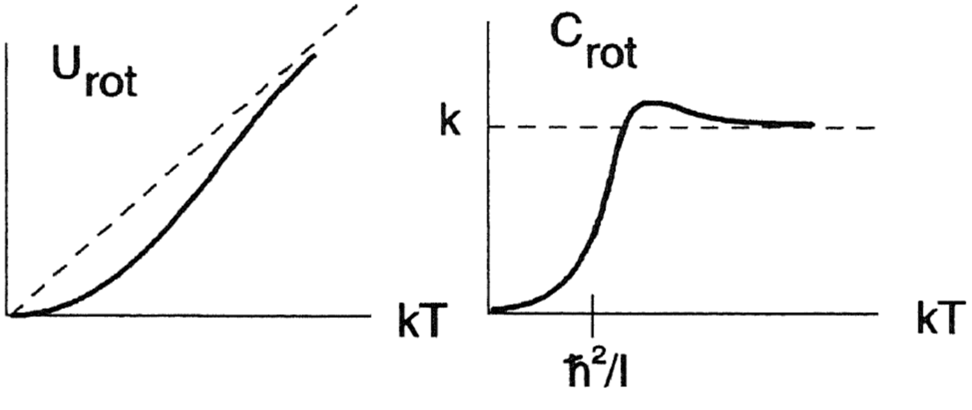
(b)

$$\begin{aligned}Q_{\text{rot}} &\approx \int_0^\infty d\ell\, 2\ell \exp\left(-\beta\hbar^2\ell^2/2I\right) \propto .\beta^{-1}\\ U/N &\approx kT\end{aligned}$$

$$\frac{c_{\text{rot}}}{k} \approx 1$$

(c)

The internal energy rises exponentially from $T = 0$ to approach a linear behavior. The qualitative behaviors are as shown in the accompanying sketch.



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Huang Introduction to Statistical Mechanics

APPENDIX

Infrared absorption of HCl

1. Moment of inertia for diatomic molecule

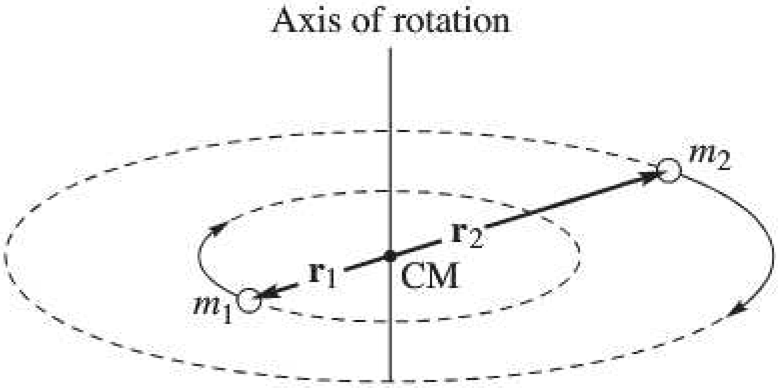


Fig. A classical model of a diatomic molecule rotating about its center of mass (Townsend)

The moment of inertia around the center of mass is given by

$$I = m_1 r_1^2 + m_2 r_2^2 .$$

From the definition of the center of mass, it is required that

$$m_1 r_1 = m_2 r_2 .$$

Suppose that the length of the bond r_0 is given by

$$r_1 + r_2 = r_0 .$$

Then we have

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}, \qquad r_2 = \frac{m_1 r_0}{m_1 + m_2} .$$

The moment of inertia is obtained as

$$I = \mu r_0^2,$$

where μ is the reduced mass and is defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

2. Evaluation of the moment of inertia in HCl

The bond length between H and Cl in HCl is

$$r_0 = 1.274 \text{ Å}.$$

The mass of H is $m(\mathrm{H}) = 1.00794$ u.
The mass of Cl is $m(\mathrm{Cl}) = 35.433$ u.

where *u* is the atomic mass unit and is given by

$$u = 1.660539 \times 10^{-24} \text{ g}.$$

The reduced mass is

$$\mu(HCl) = \frac{m(H)m(Cl)}{m(H) + m(Cl)} = 0.980061u = 1.62743 \text{ x } 10^{-24} \text{ g}$$

The moment of inertia is

$$I = \mu r_0^2 = 2.64144 \times 10^{-40} \text{ g cm}^2.$$

2. Experimental determination of *I*

The energy level related to the rotaion is given by

$$E_l = \frac{\hbar^2 l(l+1)}{2I}.$$

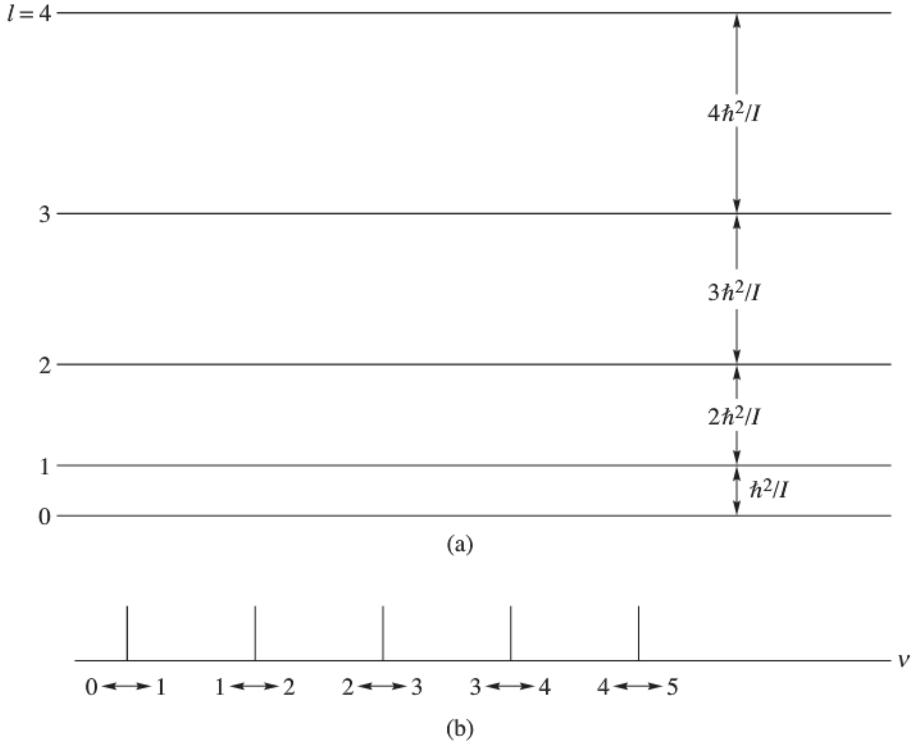


Fig. An energy-level diagram of a 3D rigid rotator. Transitions between adjacent energy levels generate the rotation spectrum (Townsend)

Figure shows the purely rotational absorption spectrum of HCl. Notice that the values of *l* are all integral.

$$\Delta E = E_l - E_{l-1} = \hbar\omega = \hbar ck = \hbar c\frac{2\pi}{\lambda}$$

or

$$\Delta E = E_l - E_{l-1} = \frac{\hbar^2 l(l+1)}{2I} - \frac{\hbar^2 l(l-1)}{2I} = \frac{l\hbar^2}{I}$$

Then we have

$$\frac{l\hbar^2}{I} = \hbar c\frac{2\pi}{\lambda},$$

or

$$\lambda l = \frac{2\pi c}{\hbar} I\,,$$

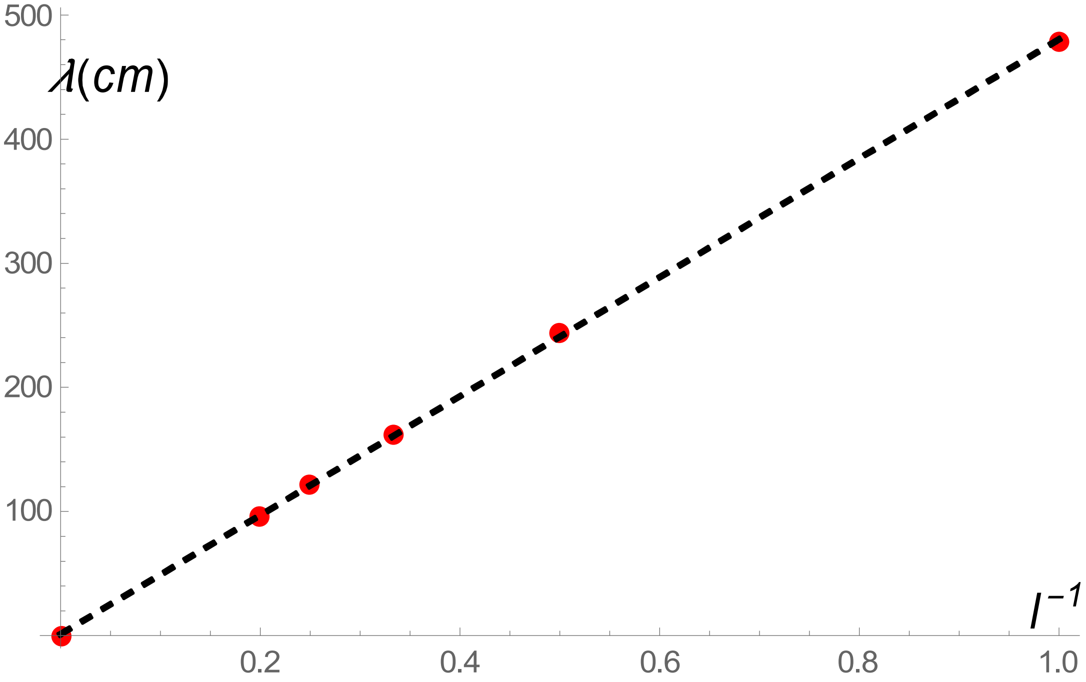


Fig. Plot of λ (cm) as a function of $1/l$. The red circles denote the experimental data. The dashed line is a least-squares fit curve.

The least squares fits of the data yields

$$\lambda = \frac{479.183 \times 10^{-4}}{l} \text{ (cm)}.$$

When $\lambda l = 0.0479183\text{cm}$ (experimental data), we have

$$I = 2.68273 \times 10^{-40} \text{ cm}^2 \text{ g}.$$

which is very close to the theoretical value

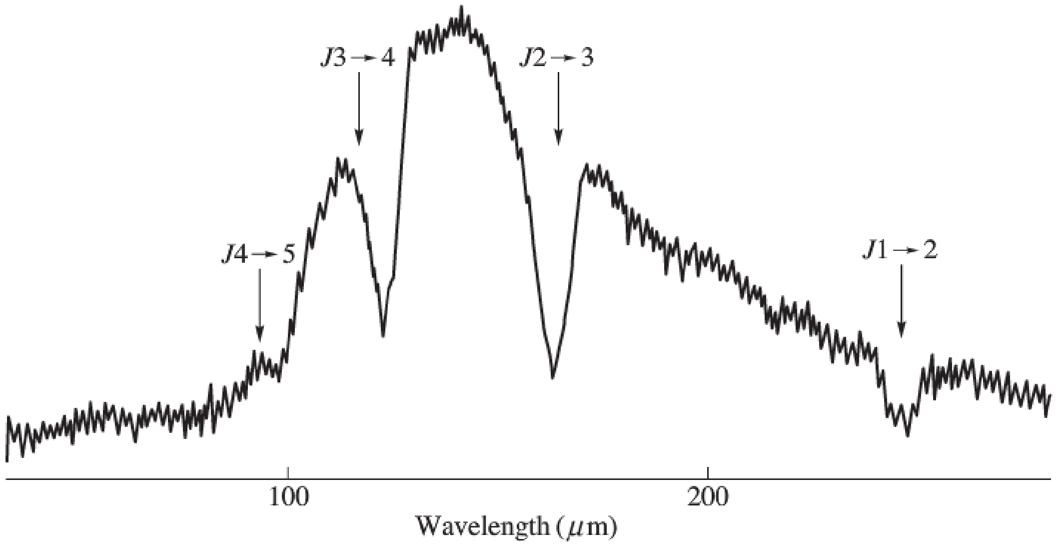


Fig. Absorption spectra of HCl (Townsend)

Transition $l-1\to l$	λ (microns)	$\nu = c/\lambda$ (10^9 Hz)	ν/l (10^9 Hz)	λl (cm)	$\lambda\nu$ (eV)
$(0\to 1)^a$	(479)	(626)	(626)	(0.0479)	(0.0026)
$1\to 2$	243	1235	618	0.0486	0.0051
$2\to 3$	162	1852	617	0.0486	0.0077
$3\to 4$	121	2479	620	0.0484	0.0103
$4\to 5$	96	3125	625	0.0480	0.0129

Table Rotational absorption transition in HCl. 1GHz= 10^9 Hz. 1 THz= 10^{12} Hz

4. Infrared absorption spectra of HCl

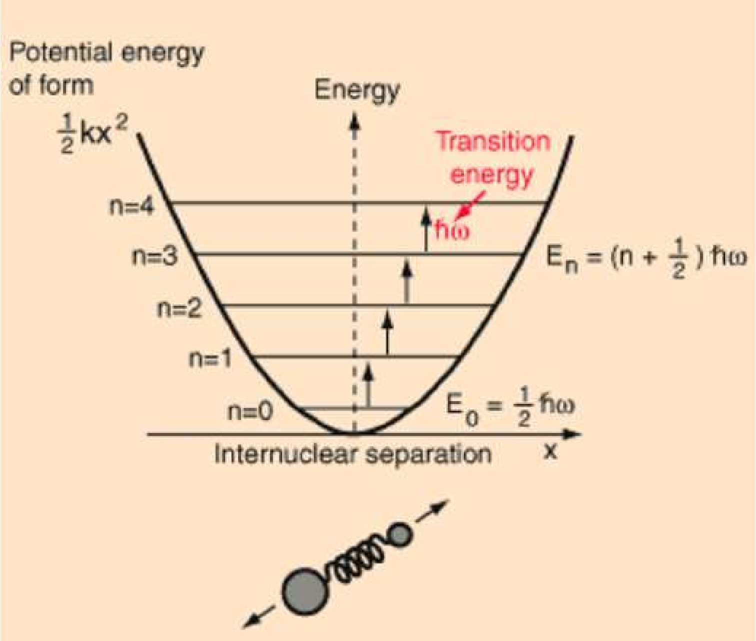


Fig. Energy level of the simple harmonics (in quantum mechanics).
http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html

The combined vibrational and rotational energy of a diatomic molecule is given by

$$E(n_v, l) = (n_v + \frac{1}{2})\hbar\omega + \frac{\hbar^2 l(l+1)}{2I}.$$

Figure shows an energy-level diagram. HCl posseses a permanent dipole moment. There is a vibrational selection rule

$$\Delta n_v = \pm 1,$$

for electric dipole transitions. In addition, the rotational selection rule, $\Delta l = \pm 1$ leads to the set of allowed vibration-rotation frequencies. Note that the state $|l, m\rangle$ has the parity $(-1)^l$. The state $|n_v\rangle$ has the parity $(-1)^n$.

The center frequency for $n_v = 0$ to $n_v=1$.

$$f = \frac{\omega}{2\pi} = 8.66 \times 10^{13}\,\text{Hz} = 86.6\text{ THz}$$

where

1 THz= 10^{12} Hz

Since $\omega = \sqrt{\dfrac{k}{\mu}}$, we can determine the force constant for the simple harmonics, as

$$k = \mu\omega^2 = \mu(2\pi f)^2 = 4.81834 \text{ x } 10^5 \text{ dyne/cm} = 480.1834 \text{ x } 10^3 \text{ N/m}$$

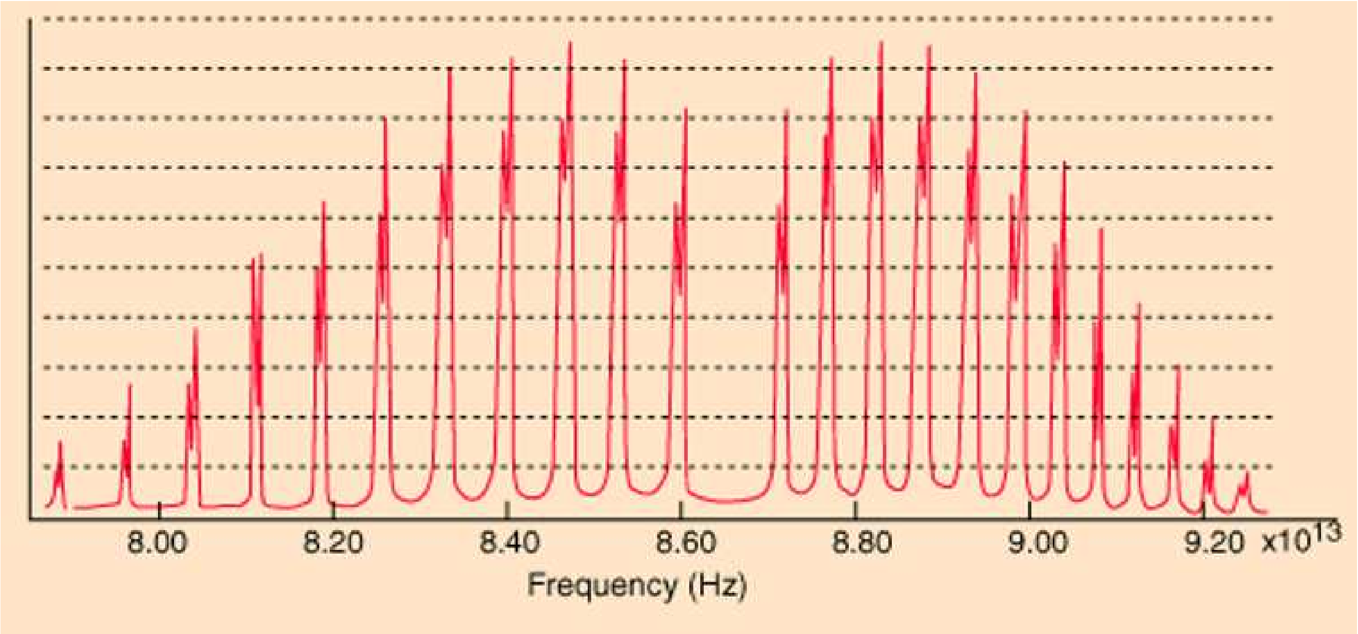


Fig. Infrared absorption of HCl.
http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html

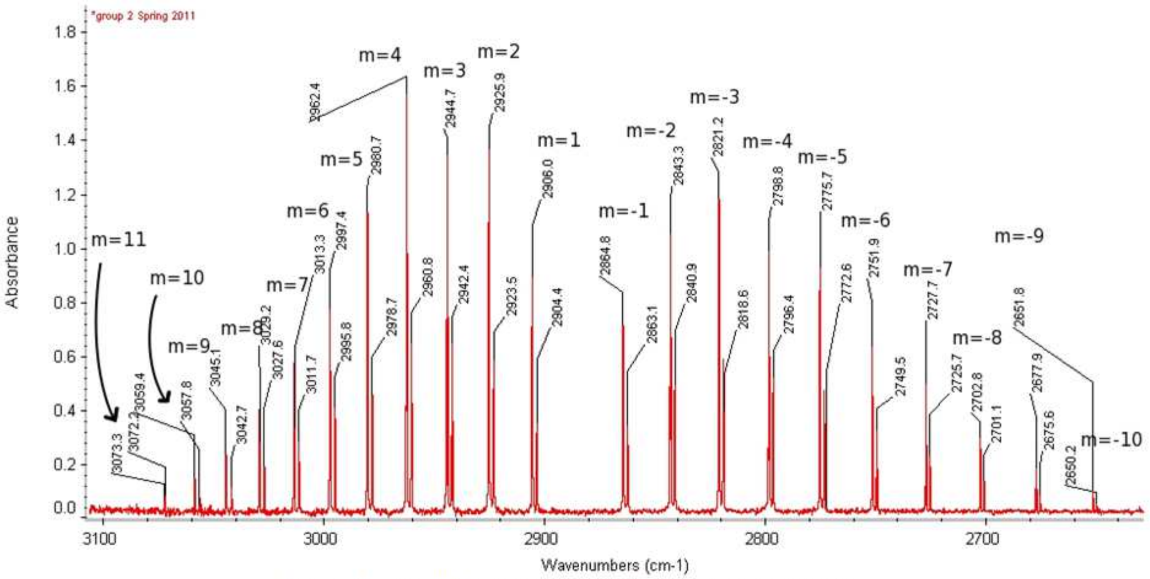
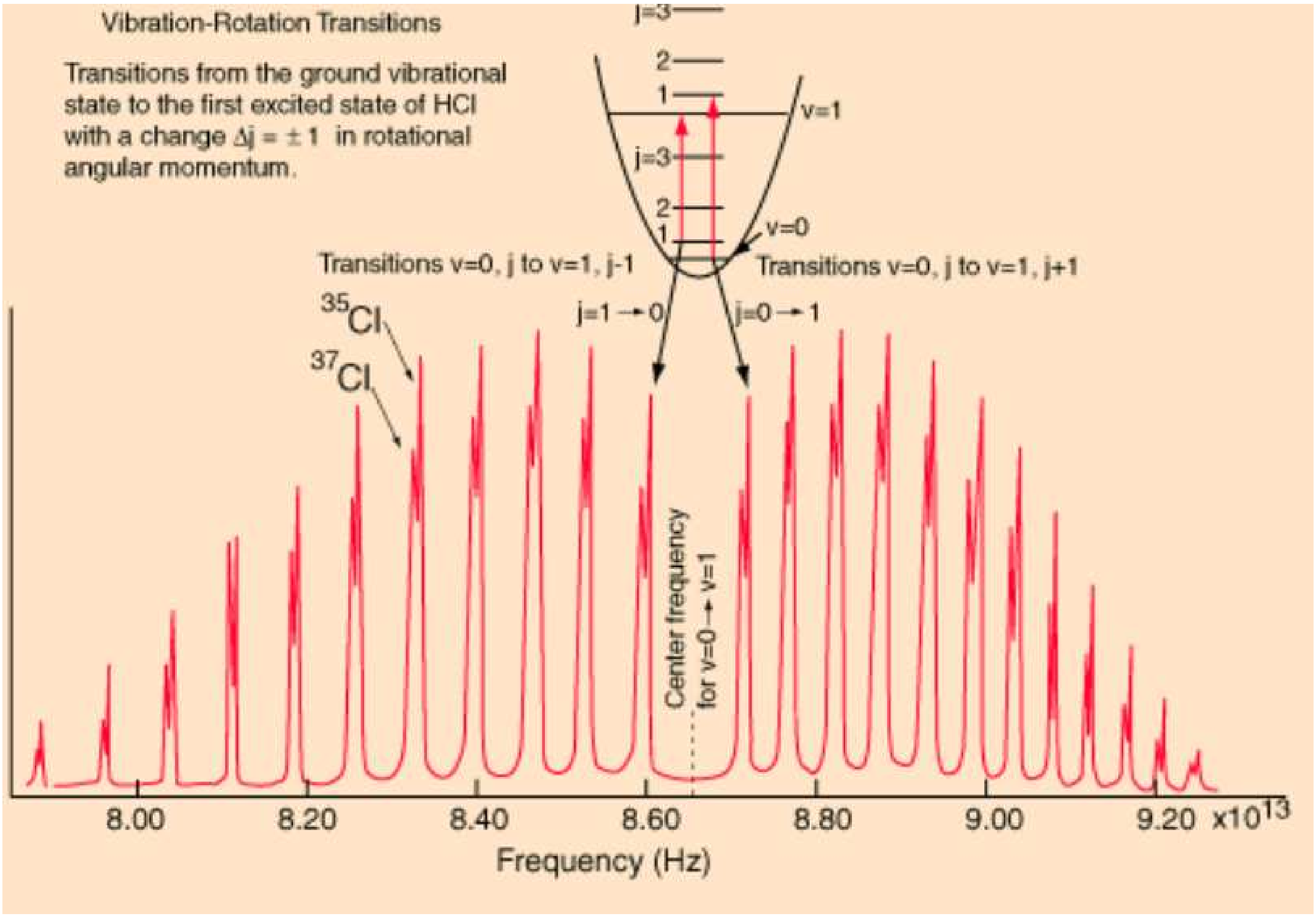
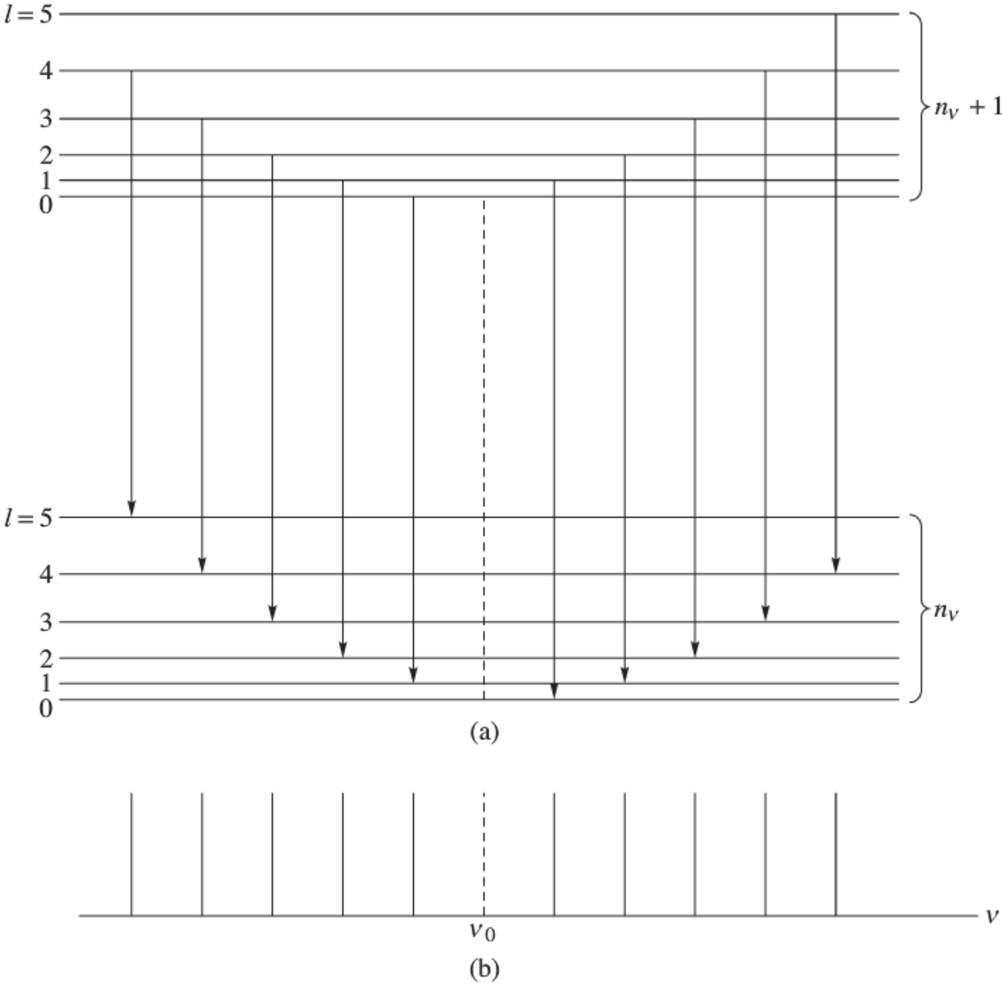


Figure 1: The HCl spectrum in the mid-infrared region

http://www.odinity.com/wp-content/uploads/2014/04/HCl-Spectrum.png



http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html



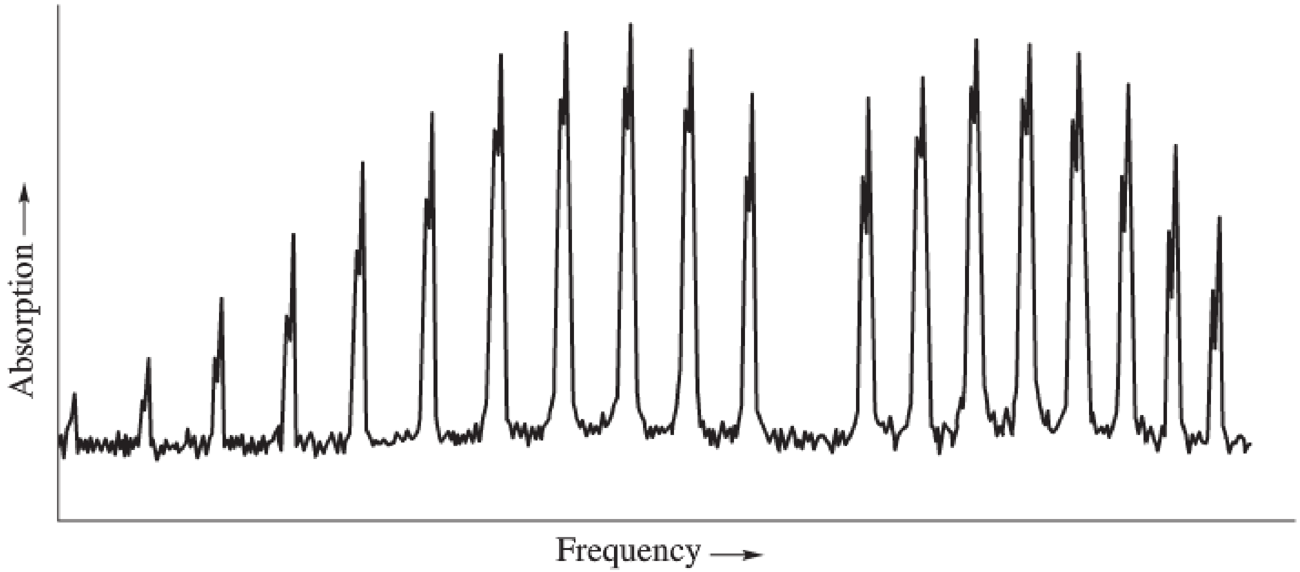


Fig. A vibrational-rotational absorption spectrum of HCl (Townsend).

5. Intensity ratio

$$k_B T = 25.852 \text{ meV} \qquad (T = 300 \text{ K}),$$

$$\hbar\omega = 0.3581 \text{ eV},$$

$$\exp(-\frac{\hbar\omega}{k_B T}) = 9.62436\times 10^{-7}.$$

Intensity for the transition from ($n_{\mathrm{v}} = 1, l\text{-}1$) state to ($n_{\mathrm{v}} = 0, l$) state is given by

$$I(l) = (2l+1)\exp[-\frac{\hbar^2 l(l+1)}{2Ik_B T}] = (2l+1)\exp[-\frac{l(l+1)B}{k_B T}],$$

where

$$B = \frac{\hbar^2}{2I} = 2.10514 \times 10^{-15} \text{ erg}.$$

6. Maximum intensity

The maximum of the intensity is given by taking the derivative of $I(l)$ with respect to l, From

$$\frac{dI(l)}{dl} = \exp[-\frac{l(l+1)}{k_B T}B][\frac{2k_B T - B(1+2l)^2}{k_B T}] = 0\,.$$

$I(l)$ has a peak at

$$2l+1 = \sqrt{\frac{2k_B T}{B}} = 6.273 \qquad \text{or} \qquad l = 2.63.$$

when $T = 300$ K and $B = \frac{\hbar^2}{2I}$=2.10514 x 10^{-15} erg.

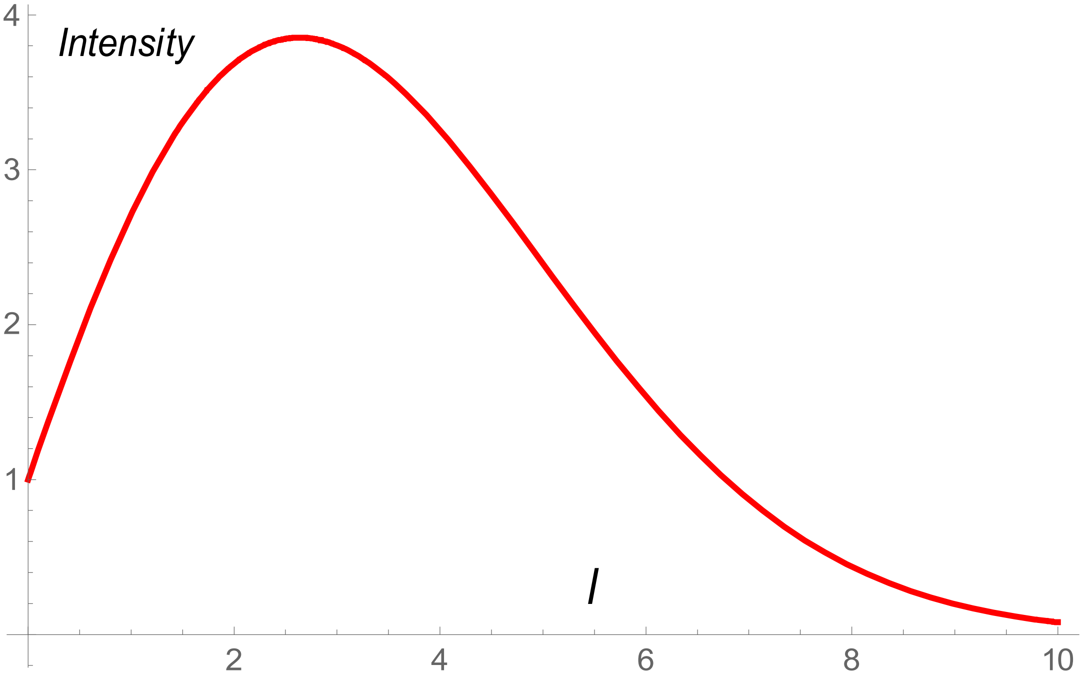


Fig. Intensity $I(l) = (2l+1)\exp[-\frac{l(l+1)}{k_B T}B]$ as a function of l. T = 300 K. $B = \frac{\hbar^2}{2I}$=2.10514 x 10^{-15} erg

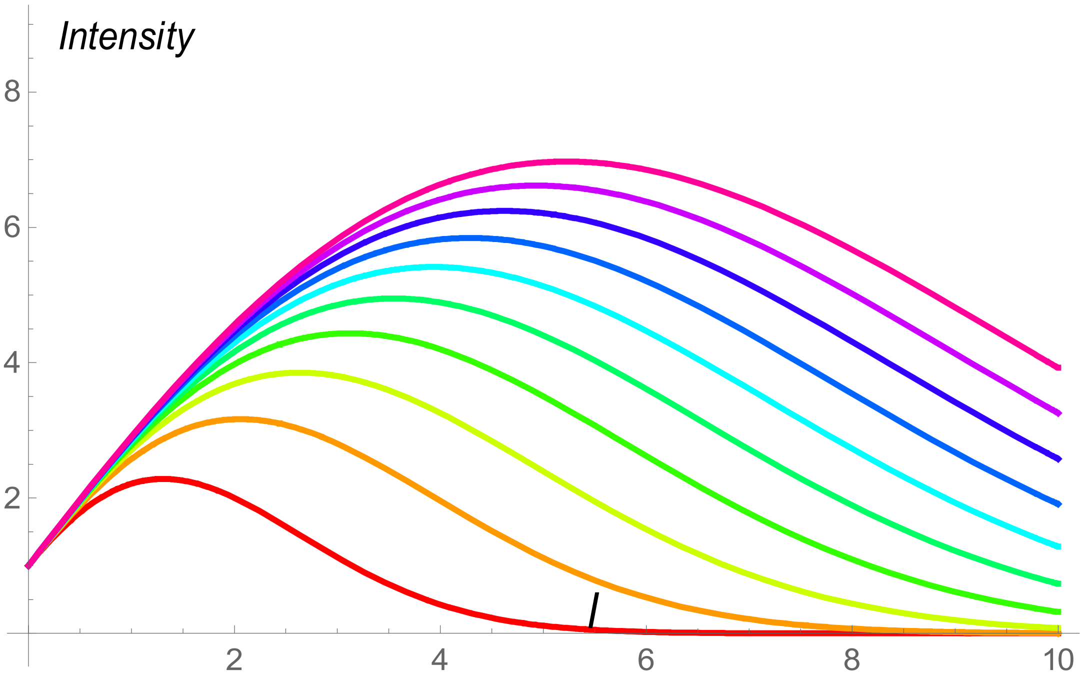


Fig. Intensity vs l where T is changed as a parameter. T = 100 K (red), 200 K, 300 K, 400, K,…, 900 K (purple), and 1000 K. The peak position of *l* shifts to the higher side as *T* increases.

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