

Infrared absorption in HCl
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Here we discuss the vibration and rotations of a diatomic molecules such as HCl, based on the experimental results on the infrared absorption spectra.

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. For a given sample which may be solid, liquid, or gaseous, the method or technique of infrared spectroscopy uses an instrument called an **infrared spectrometer** (or spectrophotometer) to produce an **infrared spectrum**. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1} .

http://en.wikipedia.org/wiki/Infrared_spectroscopy

1. Moment of inertia for diatomic molecule

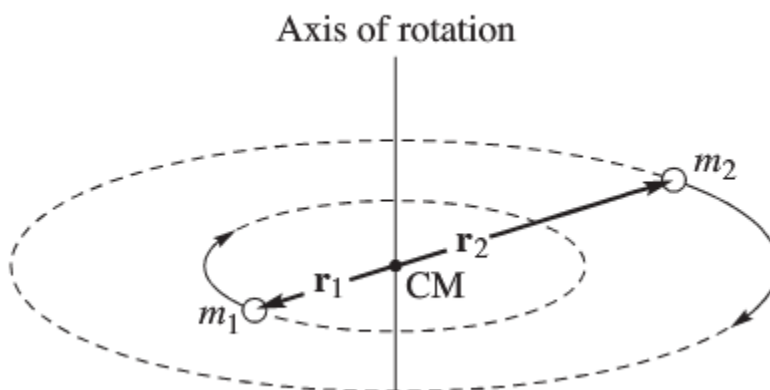


Fig. A classical model of a diatomic molecule rotating about its center of mass (Townsend)

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

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

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

$$r_0 = 1.274 \text{ \AA} .$$

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

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

where u is the atomic mass unit and is given by

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

The reduced mass is

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

The moment of inertia is

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

3. Experimental determination of I

The energy level related to the rotation is given by

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

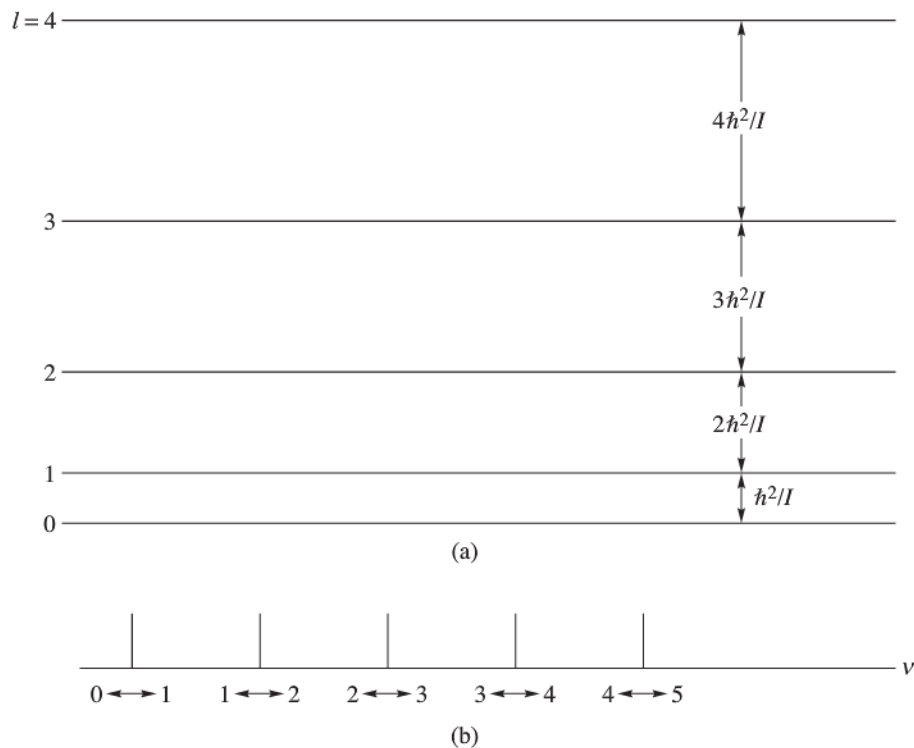


Fig. An energy-level diagram of a 3D rigid rotator. Transitions between adjacent energy levels generate the rotation spectrum (Townsend)

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

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

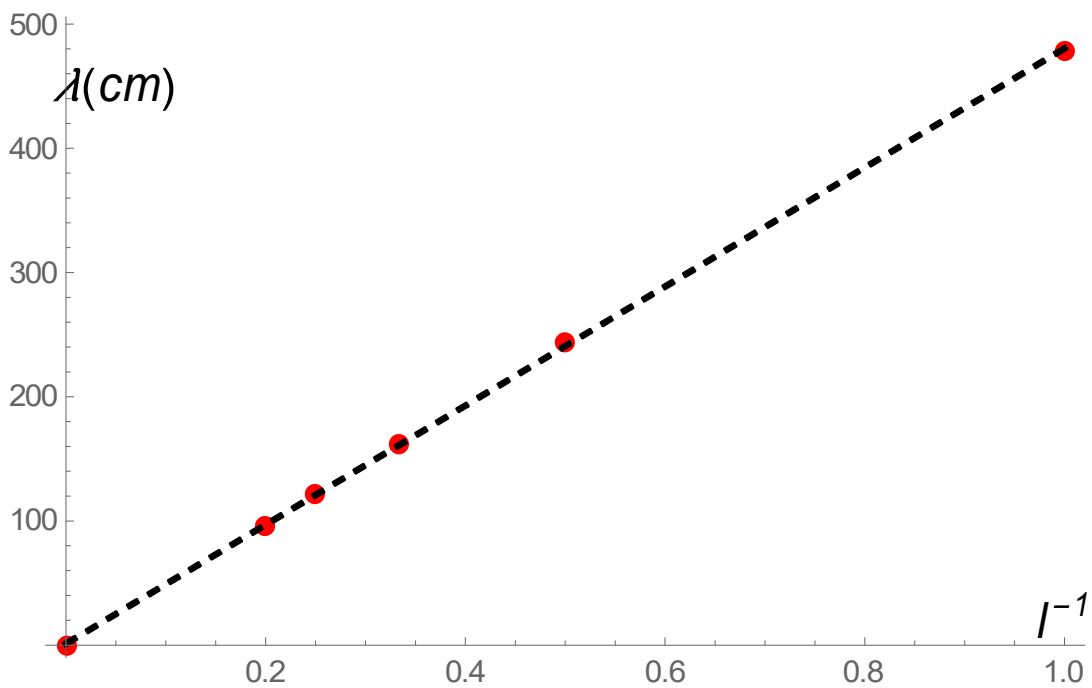


Fig. Plot of λ (cm) as a function of $1/l$. The red circles denote the experimental data. The dashed line is a least-squares fit curve.

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

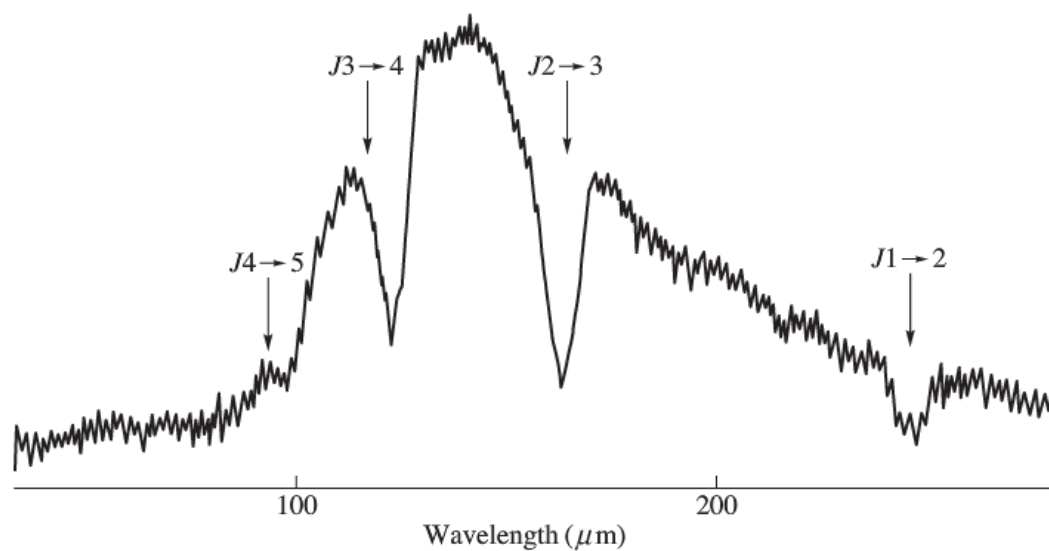


Fig. Absorption spectra of HCl (Townsend)

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

Table Rotational absorption transition in HCl.

4. Infrared absorption spectra of HCl

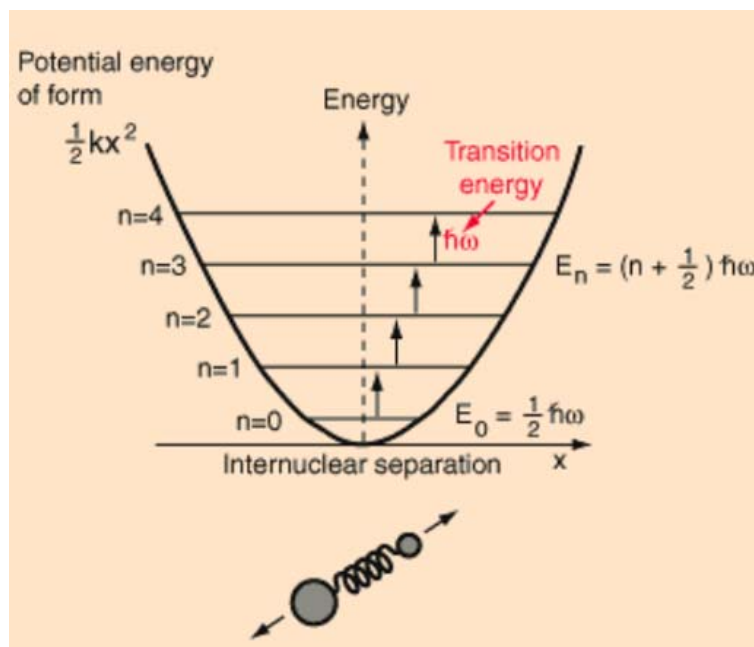


Fig. Energy level of the simple harmonics (in quantum mechanics).

<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 possesses a permanent dipole moment. There is a vibrational selection rule

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

for electric dipole transitions. In addition, satisfying 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 $(-1)^{n_v}$.

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

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

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

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

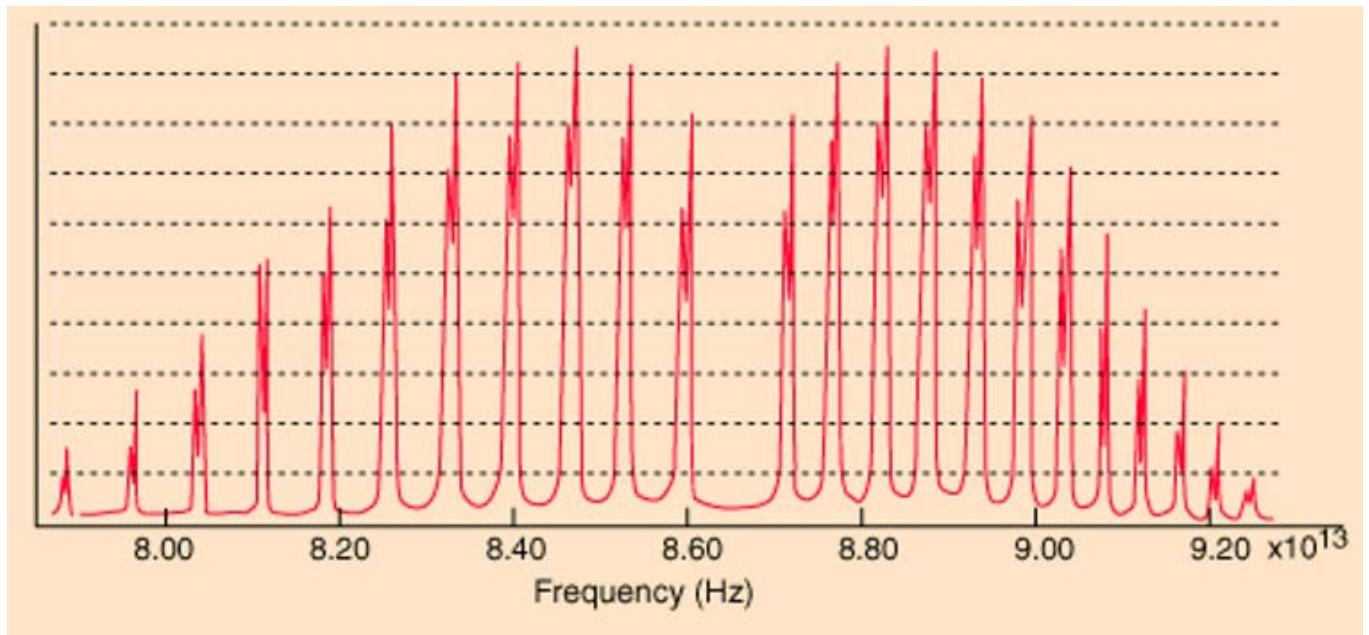
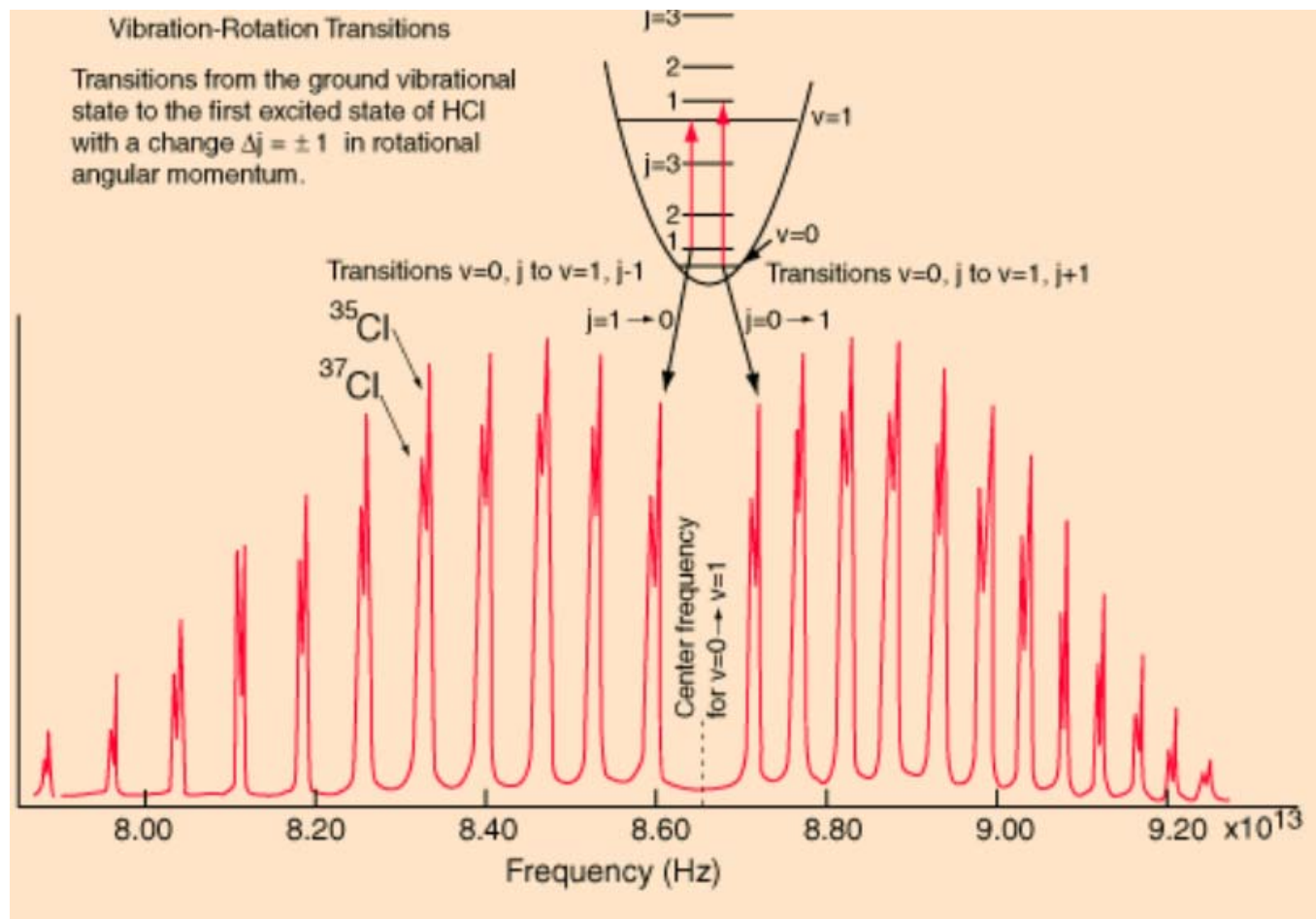


Fig. Infrared absorption of HCl.

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



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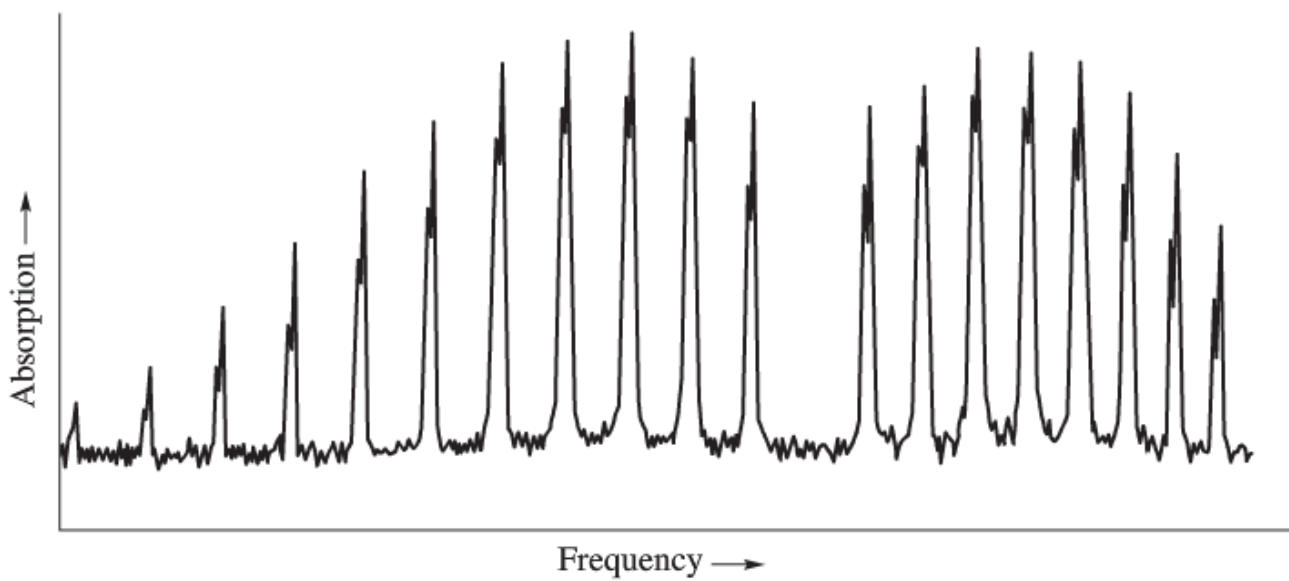
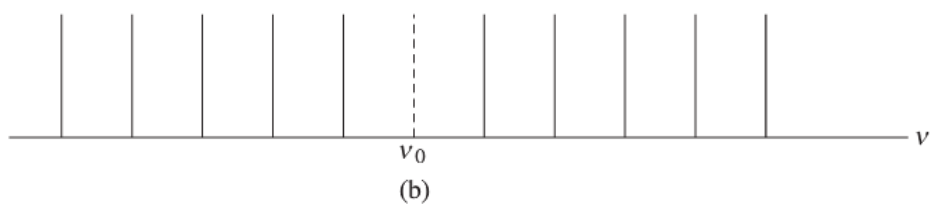
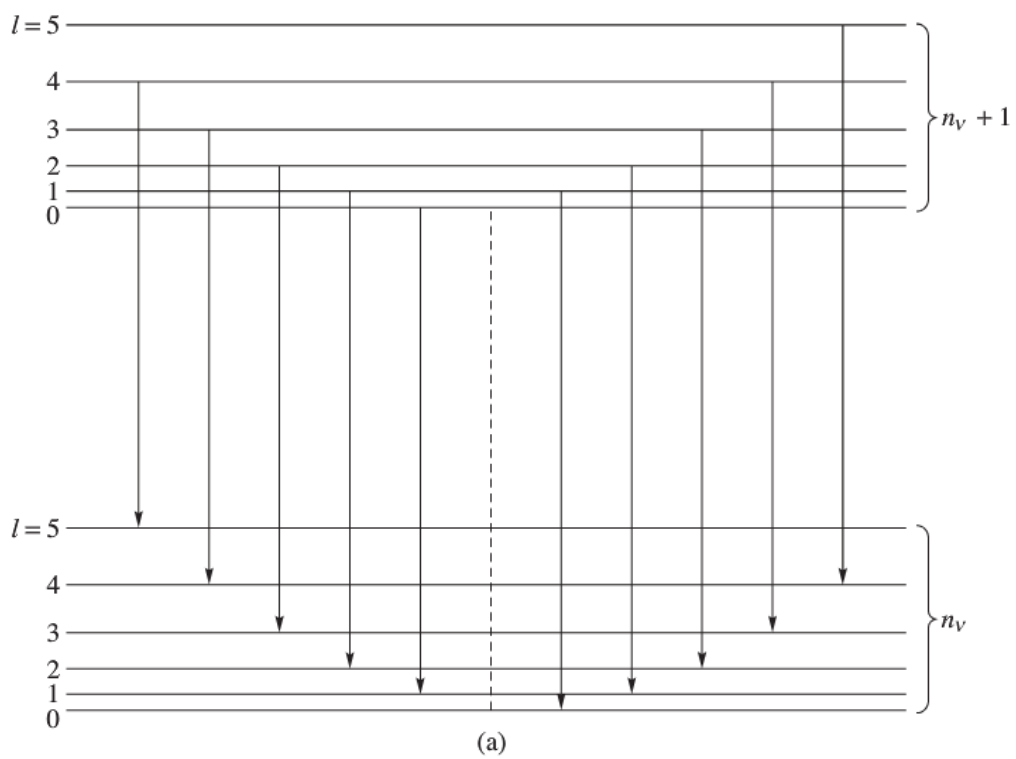


Fig. A vibrational-rotational absorption spectrum of HCl (Townsend).

5. Intensity ratio

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

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

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

Intensity for the transition from $(n_v = 1, l-1)$ state to $(n_v = 0, l)$ state is given by

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

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

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

$I(l)$ has a peak at

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

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

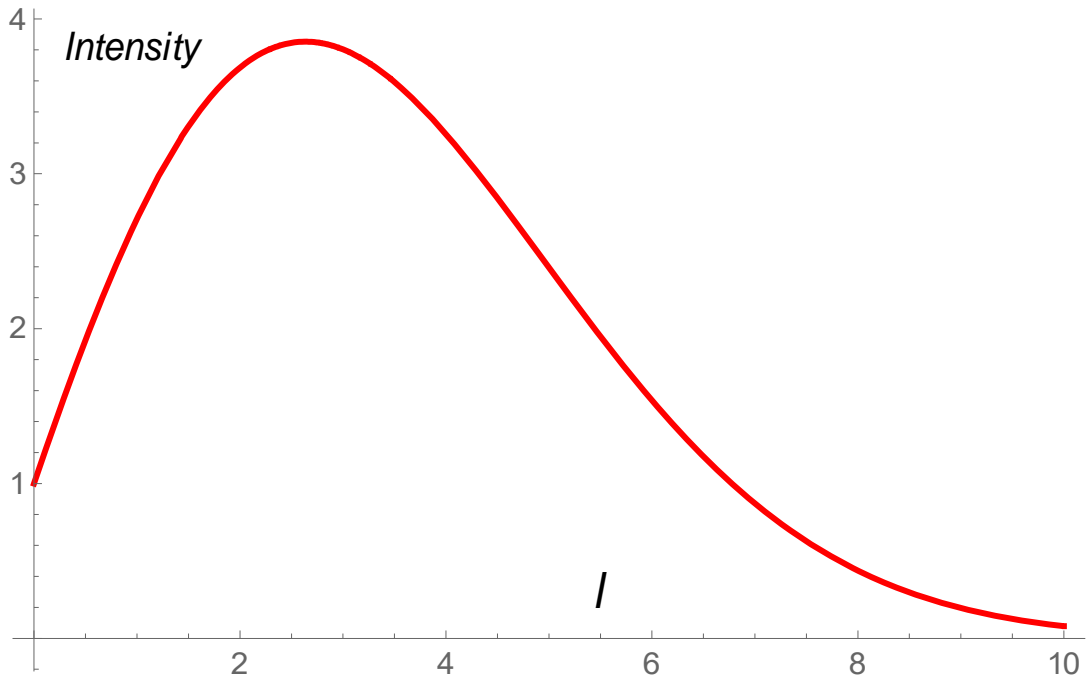


Fig. Intensity $I(l) = (2l + 1) \exp\left[-\frac{l(l+1)}{k_B T} B\right]$ as a function of l . $T = 300$ K. $B = \frac{\hbar^2}{2I} = 2.10514 \times 10^{-15}$ erg

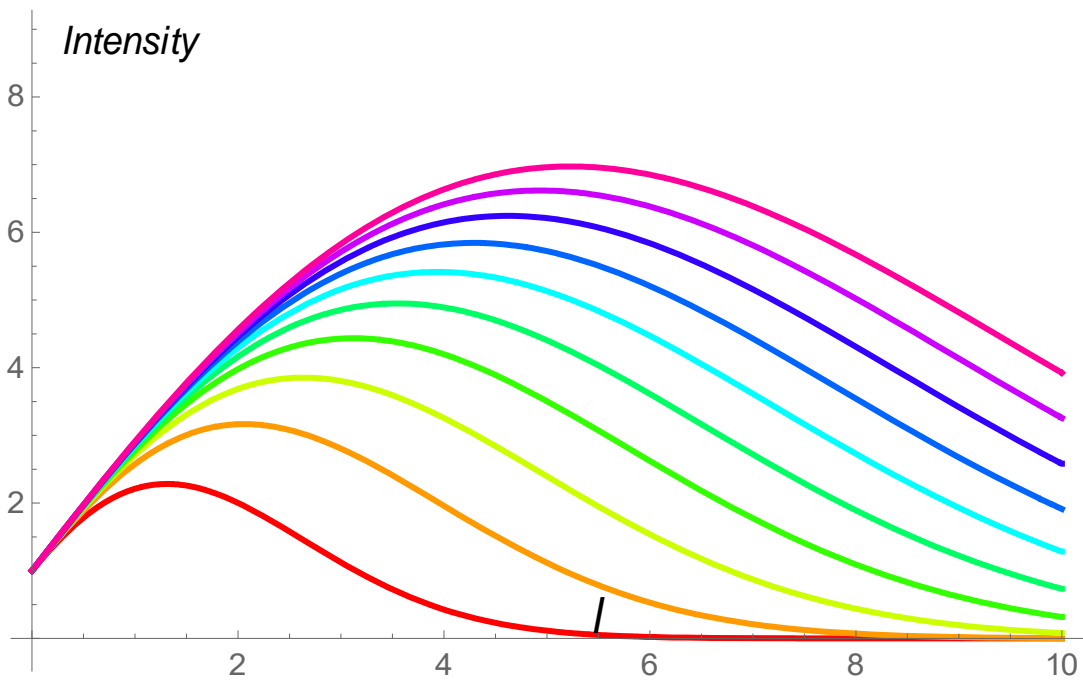


Fig. Intensity vs l where T is changed as a parameter. $T = 100$ K (red), 200 K, 300 K, 400, K, ..., 900 K (purple), and 1000 K. The peak position of l shifts to the higher side as T increases.

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