5.1 Boltzmann distribution of molecules over the energy levels

In experiments designed to measure properties of individual molecules we always work with a macroscopic sample (in a closed container) containing a very large number, N_{tot}, of identical molecules, and usually at room temperature. The sample is usually a gas under "ideal gas conditions", because it is necessary to minimize intermolecular interactions; otherwise we could not assume that the molecules are independently moving. Nevertheless, the molecules in the sample are continuously colliding with each other so that a molecule in a low energy level at one instant may be excited into a higher energy level a moment later. It is obviously not possible to keep track of the energy level of a given molecule, but when thermal equilibrium in the macroscopic sample is reached we expect that the average number of molecules at each energy level will be constant in time. An important property of a macroscopic system in thermal equilibrium is its absolute temperature T. The average number of molecules with energy E_j in the sample at a given T is called the "population" of the one-molecule energy level E_j.[1]

The population N_j of a molecular energy level E_j in a sample which is in thermal equilibrium at absolute temperature T is given by the Boltzmann distribution law:

$$N_j = C g_j e^{-E_j/k_B T}$$ Boltzmann distribution   eq 5.1

where C is a constant that is the same for all energy levels, g_j is the degeneracy of the energy level E_j, and k_B is the Boltzmann constant. The latter is the gas constant per molecule:

$$k_B = R/N_A = 1.38065 \times 10^{-23} \text{ J/K}.$$ eq 5.2

The exponential, $e^{-E_j/k_B T}$, in eq 5.1 is called the "Boltzmann factor". Let us label the energy levels as E_1, E_2, …, starting with the ground level, and in increasing order of energy. Then the population of the jth energy level relative to that of the ground level is

$$\frac{N_j}{N_1} = \frac{g_j}{g_1} e^{-(E_j - E_1)/k_B T}$$ eq 5.3

This expression shows that at absolute zero, $T=0$, only the ground state will have a nonzero population; i.e. all molecules in the sample will be in the ground energy level E_1 at absolute zero. At higher temperatures, excited energy levels can also be populated. The extent of population of an excited level E_j depends critically on the value of the positive dimensionless ratio, $(E_j - E_1)/k_B T$, in the exponential of eq 5.3.[2] The term $k_B T$ has energy units, and is a measure of average <u>thermal energy per molecule</u>. Only when the energy of the jth level relative to the ground state, (E_j-E_1), is not too large relative to $k_B T$, the level may have a significant population. In particular, populations of highly excited levels are negligible at the usual temperatures employed in experiments.

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[1] The concept of "population" of a one-molecule energy level is similar to "occupation numbers" discussed previously. It is the <u>average</u> occupation number of a level at temperature T.
[2] For <u>positive</u> x values, the exponential function e^{-x} very rapidly approaches zero as x increases.

Wavenumber unit for frequency and energy. From the relation $\nu\lambda = c$ for a photon, we may write

$$\nu = c\tilde{\nu} \qquad \text{Conversion between } cm^{-1} \text{ and } Hz \text{ units of frequency} \qquad\qquad \text{eq 5.4}$$

where $\tilde{\nu} = 1/\lambda$ is called the "wavenumber". The SI unit of $\tilde{\nu}$ is m^{-1}, but it is conventional to use cm^{-1}, instead. We will follow this practice and use the cm^{-1} unit in what follows. The speed of light in eq 5.4 must then be in cm/s unit, i.e. $c=2.998\times10^{10}$ cm/s.

The relation in eq 5.4 may be regarded as a conversion from one unit of frequency to another one. Thus the symbol $\tilde{\nu}$ on the right side can be viewed as the frequency of a photon in the cm^{-1} unit, whereas ν on the left side as the same thing but in Hz (i.e. s^{-1}) unit, and c as the conversion factor between the two units of frequency. For example, a frequency of 33.4 cm^{-1} corresponds to 1×10^{12} s^{-1} by eq 5.4, and it is legitimate to write 33.4 cm^{-1} = 1×10^{12} s^{-1}. This idea of using cm^{-1} as a unit of frequency is generalized to the vibrational frequencies of molecules. For example, the experimentally determined vibrational frequency of the $H^{35}Cl$ molecule is universally reported as 2990.95 cm^{-1}.

The energy of a photon may be expressed in terms of the wavenumber as

$$E_{photon} = hc\tilde{\nu} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{eq 5.6}$$

This relation suggests that $\tilde{\nu}$ can also be considered as the <u>energy</u> of the photon, but in cm^{-1} unit, the conversion factor to the joule unit being hc. Thus cm^{-1} can be used either as a unit of frequency or as a unit of energy, with conversion factors of c and hc, respectively, to the SI units. Whether frequency or energy is meant is inferred from the context in which it is used. Thus, it is not uncommon to read in textbooks that a certain photon has an <u>energy</u> of e.g. 33.4 cm^{-1}. This usage of cm^{-1} as a unit of energy is generalized to the energies of material particles

$$E = hc\tilde{\nu} \qquad \text{Conversion between } cm^{-1} \text{ and SI units of energy} \qquad\qquad \text{eq 5.7}$$

In any calculation involving several terms, it is necessary to do conversions only when one or more terms have different units. As an example, let us consider the rotational energy levels of the $H^{35}Cl$ molecule: $E_J=BJ(J+1)$ where $B=10.397$ cm^{-1} is an energy quantity. If we want to calculate, $\frac{E_J - E_0}{k_B T} = \frac{E_J}{k_B T}$, needed in the Boltzmann factors, say at a temperature of $T=300$ K, for several values of J, we may first calculate $k_B T$ in cm^{-1} by $1.381\times10^{-23}(300)/hc = 208.6$ cm^{-1}, and then proceed; instead of converting B into joules and employing the value of $k_B T$ in joules.

$$\frac{E_J}{k_B T} = \frac{B}{k_B T}J(J+1) = \frac{10.397}{208.6}J(J+1) = aJ(J+1), \qquad a = 0.0498$$

The degeneracy of rotational level E_J is 2J+1. Thus the relative populations of the rotational levels at $T=300$ K are

$$\frac{N_J}{N_0} = (2J+1)e^{-aJ(J+1)}, \quad J = 0,1,2,\dots$$

Table 5.1 Relative populations of rotational levels of $H^{35}Cl$ molecules at $T=300$ K. $B=10.397$ cm^{-1}.

J	0	1	2	3	4	5	6	7	8	9
N_J/N_0	1	2.715	3.707	3.849	3.321	2.465	1.602	0.920	0.470	0.214

5.2 Selection rules in transitions between rotational levels

When our sample of $H^{35}Cl$ molecules is irradiated with light in the microwave (MW) region, photons can be absorbed by the molecules; a molecule that is initially in a rotational level E_J may be excited into a higher energy level $E_{J'}$ after absorbing a photon of energy equal to ($E_{J'}$-E_J). It can be shown that in light absorption, only those transitions where

$\Delta J=\pm1$ Selection rule in rotational transitions   eq 5.8

are allowed. In MW absorption (i.e. in "pure" rotational transitions) the plus sign applies so that only the $J \rightarrow J+1$ transitions are permitted.[3] Thus the possible energies of MW photons that can be absorbed by this sample are given by

$$E_{J+1} - E_J = 2B(J + 1), \quad J = 0,1,2, \dots$$ eq 5.9

Table 5.2 MW absorption by a sample of $H^{35}Cl$ molecules at $T=300$ K. $B=10.397$ cm^{-1}.

$J_{initial}$	0	1	2	3	4	5	6	7	8	9
N_J/N_0	1	2.715	3.707	3.849	3.321	2.465	1.602	0.920	0.470	0.214
$h\nu_{photon}$	2B	4B	6B	8B	10B	12B	14B	16B	18B	20B
ν_{photon}/cm^{-1}	20.79	41.59	62.38	83.18	104.0	124.8	145.6	166.4	187.1	208.0

Relative intensities of the absorption lines are directly proportional to the relative populations of the <u>initial</u> rotational levels. Thus the most intense absorption occurs with light of frequency $8B=83.18$ cm^{-1} (Figure 5.1).
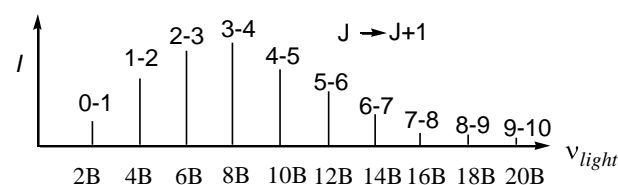

Figure 5.1 Rotational absorption spectrum of a sample of $H^{35}Cl$ molecules at $T=300$ K. Note that absorption lines are equidistant with a spacing of $2B=20.79$ cm^{-1}.

Not every diatomic molecule absorbs MW radiation. There is a gross selection rule which states that only <u>polar</u> molecules undergo rotational transitions. Thus homonuclear diatomics such as H_2, O_2, etc. have no rotational absorption spectra (i.e. they are transparent to MW radiation).

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[3] We will see later that light absorption can cause a simultaneous excitation in rotational as well as vibrational levels of a molecule. In such a case which requires (IR) photons with larger energies than here, both signs in eq 5.8 must be considered. Here, we are assuming that the vibrational level is not changing in the absorption process.
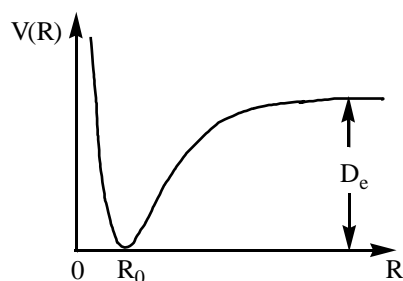
5.3 Vibrational energy levels of a diatomic molecule

Vibrational motion of a diatomic molecule *AB* is defined as the motion of the two atoms along the line joining them under the constraint that the *c.m.* is fixed at a point in space (Figure 5.2).
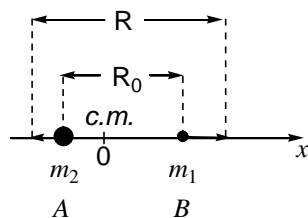
Figure 5.2 The small arrows attached to the masses indicate their new positions when the equilibrium distance, R_0, between them is altered to R. In the figure $R>R_0$, but it is also possible that $R<R_0$ in which case the directions of the small arrows should be reversed.

The attractive potential energy, *V(R)*, between the two atoms in a diatomic molecule is a function of the distance R between them. The shape of a typical vibrational potential energy is shown in Figure 5.3. It takes its minimum value at the equilibrium bond length, R_0. For a given molecule, *V(R)* is obtained by solving the Schrödinger equation for the electrons in the molecule as a function of the internuclear distance *R*, as will be discussed later in this course. For now, we assume that the function *V(R)* for the particular diatomic molecule under study is given to us.

Figure 5.3 Vibrational potential energy curve for a diatomic molecule; D_e is the "electronic" dissociation energy of the molecule.

5.3.1 Harmonic approximation

The function *V(R)* can be expanded into a Taylor series about the point R_0 as follows:

$$V(R) = V(R_0) + V'(R_0)((R - R_0) + \frac{1}{2}V''(R_0)(R - R_0)^2 + \frac{1}{6}V'''(R_0)(R - R_0)^3 + \cdots \quad \text{eq 5.10}$$

The first term, $V(R_0)$, is a constant which we take as zero, and the second term is zero since the first derivative $V'(R_0)=0$ at the minimum of *V*. Letting $x = R - R_0$, and assuming that the terms involving third and higher derivatives in eq 5.10 could be neglected as giving small corrections, one obtains the "harmonic approximation" to the true *V*:

$$V_h(x) = \frac{1}{2}kx^2 \qquad \text{Harmonic potential} \qquad \qquad \text{eq 5.11}$$

where

$k=V''(R_0)$ Force constant   eq 5.12

is called the "force constant". The SI unit of k is N/m, or equivalently J/m^2. The significance of the harmonic approximation is that with V_h the vibrational Schrödinger equation can be solved <u>analytically</u>.[4] Results will be given below.

It is shown in the appendix that the classical Hamiltonian for the vibrational motion in the harmonic approximation is

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$ eq 5.13

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass. Classically $H=E$ where the vibrational energy E is a constant of the motion. At a given E, the classical motion is vibration (also called "oscillation") between the turning points $-x_t$ and x_t with the frequency (Figure 5.4)
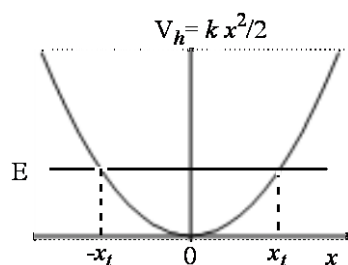
Figure 5.4 Classically at a given E, $|x|$ can not exceed $|x_t|$. The physical motion is oscillation between the two turning points.

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$ Classical frequency of vibration   eq 5.14

Note that ν_e is the same at all energies E, but x_t increases as E increases. A particle with the Hamiltonian of eq 5.13 is called a "harmonic oscillator".

5.3.2 The Quantum Mechanical Harmonic Oscillator

The quantum mechanical Hamiltonian operator follows from eq 5.13 by the operator replacement:
$$p \rightarrow \hat{p} = -i\hbar\frac{d}{dx}$$

---

[4] The vibrational Schrödinger equation using the exact $V(R)$ can always be solved by numerical methods. However, analytical solutions are conceptually much more illuminating than numerical results because they are easily applicable to all diatomic molecules whereas in the numerical method one needs to do a separate calculation for each specific molecule.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}kx^2$$ eq 5.15

and the Schrödinger equation for the vibrational energy levels of a diatomic molecule in the harmonic approximation is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$$ eq 5.16

The solution of this equation is too complicated to discuss here. We will quote the results from the literature. It is found that well-behaved solutions for ψ (see Lecture Notes 2, Section 2.3) exist only for a special set of quantized energies given by

$$E_v = \varepsilon_o\left(v + \frac{1}{2}\right), \quad v = 0,1,2,\ldots$$ eq 5.17

where

$$\varepsilon_o = h\nu_e = \hbar\sqrt{\frac{k}{\mu}}$$ eq 5.18

is a characteristic property of the diatomic molecule with energy units. The allowed vibrational energies are shown in Figure 5.5. The energy levels are equidistant with a spacing of ε_o between neighboring levels.
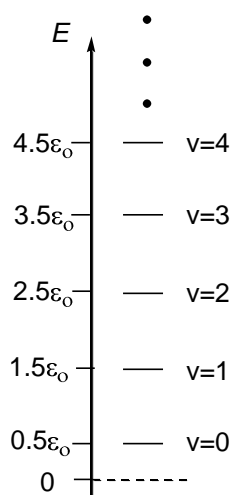
Figure 5.5 Allowed vibrational energies of a diatomic molecule in the harmonic approximation.

The lowest allowed energy is $\varepsilon_o/2$, which is also the zero point energy in the vibrational motion (ZPVE). The vibrational energies are nondegenerate; there is only one state function associated with each E_v, i.e. $g_v=1$ for all v=0,1,2,…

Example 5.1 Find the populations of vibrational levels in a sample of gaseous H^{35}Cl molecules at 300 K, given that the vibrational frequency is 2990.95 cm^{-1}.

Solution: We apply the Boltzmann expression, eq 5.17, to the vibrational levels. The populations are labeled by the vibrational quantum number v: N_v with v=0, 1, 2, …; the allowed vibrational energies are given by eq 5.17, and g_v=1. We have

$$\frac{N_v}{N_0} = e^{-\frac{\varepsilon_o}{k_B T}v}, \quad v = 0,1,2,\dots$$

As discussed above, the vibrational frequency ν_e=2990.95 cm^{-1} can be interpreted as the value of ε_o (eq 5.18) in wavenumber units for energy provided we also calculate $k_B T$ in the same units.[5] For T=300 K, we had found above that $k_B T$=208.6 cm^{-1}. Hence, $\varepsilon_o / k_B T$ = 2990.95/208.6 = 14.34. Relative population of the first excited vibrational level (i.e. v=1) is $e^{-14.34}$ = 5.93x10^{-7}. This is a very small population, and all the higher lying excited levels have much smaller populations. We conclude that in this sample at T=300 K, effectively all molecules are in their ground vibrational states (i.e. v=0 for all).

5.3.3 Vibrational wavefunctions and Quantum Mechanical tunneling

Expressions for the vibrational functions ψ_v are conveniently given in terms of the dimensionless variable *y* defined by

$y=x/\alpha$ eq 5.19

where

$\alpha=\left(\frac{\hbar^2}{k\mu}\right)^{1/4}$ eq 5.20

 has distance unit. The vibrational wavefunctions are

$\psi_v(y) = N_v\, H_v(y)\, e^{-y^2/2}, \quad N_v = \frac{1}{\pi^{1/4}(2^v v!)^{1/2}}$ (normalization constant)   eq 5.21

where the functions $H_v(y)$ are polynomials of degree v in *y*, known as Hermite polynomials in the literature. The variable *y* ranges from -∞ to +∞. For v=0, 1, 2, and 3, explicit expressions of Hermite polynomials are

$H_0(y)$=1   eq 5.22
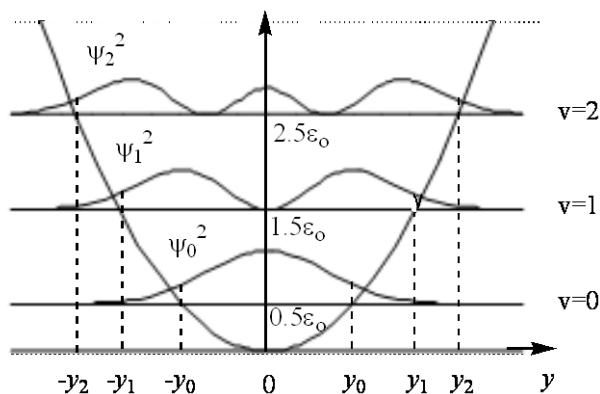
$H_1(y)$=2y   eq 5.23

$H_2(y)$=4y^2 − 2   eq 5.24

$H_3(y)$=8y^3 − 12y   eq 5.25

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[5] Alternatively, you may calculate ε_o=hc(2990.95 cm^{-1}) in Joules. In this case, you must calculate $k_B T$ in Joules, also.

Note that ψ_v are real-valued functions. Figure 5.6 shows graphs of probability densities ψ_v^2 for the lowest three vibrational states.

Figure 5.6 Probability density vs. y for the vibrational states with v=0, 1, 2. The horizontal axis for ψ_v^2 is drawn at E_v above the minimum of V_h. The points $\pm y_v$ are the classical turning points at the corresponding energy levels (see eq 5.28 below).

At a given energy, the classical harmonic oscillator is confined between the two turning points. As shown in Figure 5.6, the quantum oscillator has a nonzero probability of being in the classically forbidden region. When a particle passes into a region that is classically prohibited, the process is called "tunneling".

We can calculate the total probability of finding the particle with energy E_v (eq 5.17) in the classically forbidden region as follows. The state function associated with energy level E_v is ψ_v. The probability of finding the particle at a distance larger than the turning point y_t at this energy is given by

$$Pr(y > y_t) = \int_{y_t}^{\infty} \psi_v^2(y)dy$$
<div style="text-align: right">eq 5.26</div>

Similarly, the probability of finding the particle at points y<- y_t is

$$Pr(y <- y_t) = \int_{-\infty}^{-y_t} \psi_v^2(y)dy = \int_{y_t}^{\infty} \psi_v^2(y)dy = Pr(y > y_t)$$
<div style="text-align: right">eq 5.27</div>

because $\psi_v^2(y)$ is an even function of y (see Figure 5.6). Thus the total probability of finding the particle in the classically forbidden region is: $Pr_{tot}=2\ Pr(y > y_t)$. The turning point y_t is found by expressing V_h (eq 5.11) in the dimensionless variable y, and equating it to E_v. From eqs 5.18 and 20 we note that $\alpha^2 k = \varepsilon_o$ so that

$$V_h = \frac{1}{2}kx^2 = \frac{1}{2}\varepsilon_o y^2$$

Hence

$$\frac{1}{2}\varepsilon_o y_t^2 = \varepsilon_o \left(v + \frac{1}{2}\right)$$

or

$$y_t = \sqrt{2v+1}, \qquad v = 0, 1, 2, \dots \qquad \text{Classical turning points at energies } E_v \qquad \text{eq 5.28}$$

We have calculated the integral in eq 5.26 for the three states shown in Figure 5.6 using a computer.[6] The total probabilities of finding the particle in the classically forbidden region are: Pr_{tot}= 0.157, 0.112, and 0.095 for the states with v=0, 1, and 2, respectively. Among all allowed states, the particle in the ground state has the largest probability (15.7 %) of being found outside the parabolic potential.

5.3.4 Selection rules in vibrational transitions

The gross selection rule: Only heteronuclear diatomic molecules undergo vibrational transitions in their interactions with light. Thus homonuclear diatomic molecules such as H_2, N_2, etc. have no IR spectra.

For a heteronuclear diatomic molecule, there is a vibrational selection rule

$$\Delta v = \pm 1 \qquad\qquad\qquad \text{eq 5.29}$$

The plus sign is for absorption, and the minus sign is for emission of light by the molecule.

5.4 Vibration-Rotation Spectra of Diatomic Molecules

Thus far we treated the rotational and vibrational motions of a diatomic molecule as separate entities. The actual motion of a molecule in 3D is a simultaneous rotation coupled with vibration. It can be shown that these two types of motions are approximately independent so that the Hamiltonian for the more general motion of a diatomic molecule about its *c.m.* can be written as[7]

$$\widehat{H}_{rovib} = \widehat{H}_{rot}(\theta, \phi) + \widehat{H}_{vib}(x) \qquad\qquad \text{eq 5.30}$$

where $\widehat{H}_{rot}$ is given in eq 4.5 of Lecture Notes 4, and $\widehat{H}_{vib}$ is the vibrational Hamiltonian in eq 5.15. Since the variables in the two terms of eq 5.30 are independent, in the solution of the Schrödinger equation for simultaneous rotation and vibration, $\widehat{H}_{rovib}\,\Psi_{rovib} = E_{rovib}\,\Psi_{rovib}$, the energy is additive and the wavefunction is a product:

---

[6] The integral in eq 5.26 has an analytical result when the lower limit is zero. In other cases, the integral must be evaluated by numerical methods.

[7] The most general motion of a molecule is a simultaneous translational+rotational+vibrational+electronic motions. The translational energies and states are those of the "particle in a 3D box", and play no role in absorption or emission of light by the molecule. The electronic states will be discussed later.

$$E_{rovib} = E_{rot} + E_{vib} = BJ(J+1) + \varepsilon_o \left(v + \frac{1}{2} \right) \qquad \text{eq 5.31}$$

$$\Psi_{rovib} = Y_{JM}(\theta, \phi)\psi_v(x) \qquad \text{eq 5.32}$$

For all diatomic molecules, experiments have shown that B is much smaller than ε_o (the spacing between neighboring vibrational levels). According to eq 5.31, associated with each vibrational level there are infinitely many rotational levels, as graphically depicted in Figure 5.7.
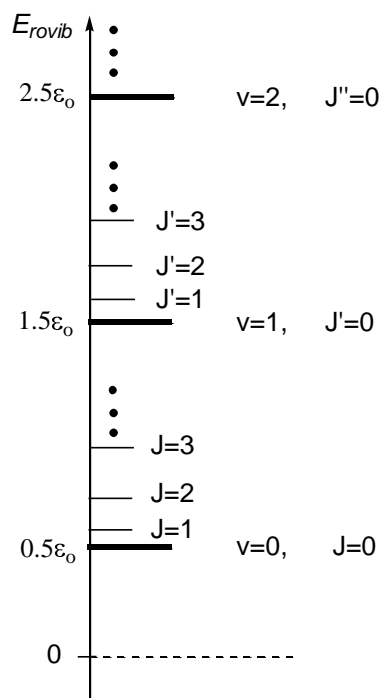
Figure 5.7 The allowed vibrational+rotational energy levels of a diatomic molecule (eq 5.31).

In its interaction with light, both the rotational as well as the vibrational state of the molecule may change, depending on the energy of the light quantum. If the photon energy is considerably smaller than ε_o, the initial vibrational state does not change ($\Delta v=0$), and only rotational transitions occur. This is the situation with "pure" rotational transitions, as discussed above. On the other hand, if the photon energy is near or above ε_o, then a vibrational transition accompanied by a rotational transition becomes possible.

Let us consider the sample of H[35]Cl molecules at 300 K. As discussed in Example 5.1, all molecules in the sample can be considered as being in the vibrational ground state: v=0. The molecules are distributed over various rotational levels belonging to the ground vibrational level, with energies given by (eq 5.31 with v=0)

$$E(v=0, J) = \frac{1}{2}\varepsilon_o + BJ(J+1), \qquad J = 0, 1, 2, \ldots \qquad \text{eq 5.33}$$

The relative populations of these levels are the same as in Table 5.1. When a molecule absorbs a photon and changes its vibrational state, due to the selection rule eq 5.29, only the level with v=1 is available as the final vibrational level. The initial rotational state must concurrently change because of the $\Delta J=\pm 1$ selection rule. In $J{\rightarrow}J+1$ transitions, energy of the molecule after absorption of a photon will be

$$E\text{(v=1, J+1)} = \frac{3}{2}\varepsilon_o + B(J+1)(J+2), \qquad J = 0, 1, 2, \ldots \qquad\qquad \text{eq 5.34}$$

so that

$$\Delta E = \varepsilon_o + 2B(J+1), \qquad J = 0, 1, 2, \ldots \qquad \text{``}J{\rightarrow}J+1 \text{ transitions''} \qquad\qquad \text{eq 5.35}$$

These vibrational+rotational transitions in which the photon energies are greater than ε_o constitute the "R branch" of the IR absorption spectrum.

It is also possible that molecules initially in rotational states with $J>0$ can undergo $J{\rightarrow}J-1$ transitions. In this case, energy of the final state will be

$$E\text{(v=1, J-1)} = \frac{3}{2}\varepsilon_o + BJ(J-1), \qquad J = 1, 2, \ldots \qquad\qquad \text{eq 5.36}$$

and hence

$$\Delta E = \varepsilon_o - 2BJ, \qquad J = 1, 2, \ldots \qquad \text{``}J{\rightarrow}J-1 \text{ transitions''} \qquad\qquad \text{eq 5.37}$$

In these transitions, energies of the absorbed photons will be smaller than ε_o; they constitute the "P branch" of the absorption spectrum.

Figure 5.8 shows one particular allowed transition in the R branch and another in the P branch, using an energy level diagram.

The full IR absorption spectrum is obtained by combining the P branch (eq 5.37) with the R branch (eq 5.35). Figure 5.9 shows the absorption spectrum of $H^{35}Cl$ at 300 K obtained in this way, for incident light frequencies in the range from 2845 cm^{-1} to 3157 cm^{-1}. Intensities of the absorption lines are proportional to the <u>initial</u> populations of the rotational levels in the ground vibrational state. Thus, intensities in the R branch are identical to those in Figure 5.1. Intensities in the P branch can be obtained from those in the R branch by noting the initial J value; e.g. intensity of the 3→2 transition in the P branch is the same as the 3→4 transition in the R branch because both intensities are proportional to the initial population of the $J=3$ rotational level. Note that there is no absorption at $\nu_{light}=\varepsilon_o$ (in cm^{-1} unit) since this transition corresponds to $\Delta J=0$ which is forbidden (see Figure 5.8).
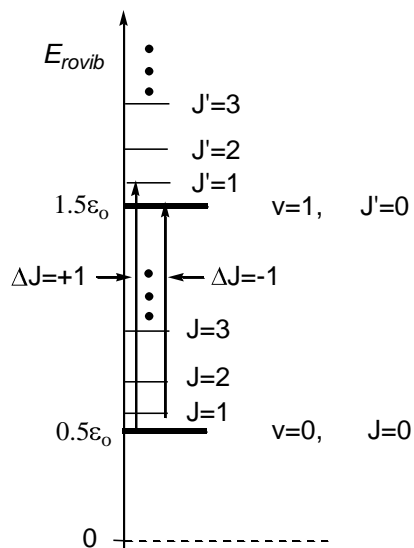
Figure 5.8 Absorptions of two different photons, both of which change the vibrational state of the molecule from the v=0 to the v=1 vibrational level. The energy of the photon leading from J=0 to J'=1 is ε_o+2B, and that of the other one causing the J=1 to J'=0 transition is ε_o-2B. The energies of these two photons differ by 4B.
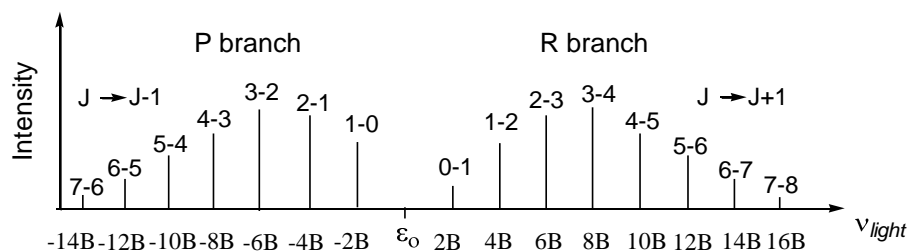
Figure 5.9 Predicted infrared absorption spectrum of H^{35}Cl at 300 K. For clarity in the graph, the energies $\varepsilon_o + 2B(J+1)$ are abbreviated as $2B(J+1)$ on the right of ε_o; similarly, $\varepsilon_o - 2BJ$ is abbreviated as $-2BJ$ on the left side of ε_o. B=10.397 cm^{-1} and ε_o=2990.95 cm^{-1}.

Appendix. Kinetic energy in the vibrational motion of a diatomic molecule

Let x_1 and x_2 be the instantaneous coordinates of the two atoms relative to the *c.m.*. In the vibrational motion, they are not independent due to the *c.m.* condition:
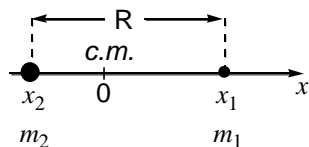
$m_1x_1+m_2x_2=0$ eq A.1

One has

$x_1-x_2=R$ eq A.2

Solving for x_1 and x_2 in terms of R, one finds

$$x_1 = \frac{m_2}{M}R, \qquad x_2 = -\frac{m_1}{M}R$$ eq A.3

where $M=m_1+m_2$. The equilibrium positions of the two atoms are obtained by setting $R=R_0$.

$$x_1^0 = \frac{m_2}{M}R_0, \qquad x_2^0 = -\frac{m_1}{M}R_0$$ eq A.4

Using eqs A.3-4, "displacements" of the two atoms from their equilibrium positions are

$$x_1 - x_1^0 = \frac{m_2}{M}x, \qquad x_2 - x_2^0 = -\frac{m_1}{M}x$$ eq A.5

where $x=R-R_0$. The velocities of the two atoms (relative to the *c.m.*) are then

$$\dot{x}_1 = \frac{m_2}{M}\dot{x}, \qquad \dot{x}_2 = -\frac{m_1}{M}\dot{x}$$ eq A.6

The kinetic energy of the vibrational motion is

$$T = \frac{1}{2}m_1\dot{x}_1^2 + \frac{1}{2}m_2\dot{x}_2^2 = \frac{1}{2}\mu\dot{x}^2, \qquad \mu = \frac{m_1m_2}{m_1+m_2}, \text{ (reduced mass)}$$ eq A.7

For the quantum mechanical Hamiltonian, we need T in terms of the (relative) momentum, $p = \mu\dot{x}$

$$T = \frac{p^2}{2\mu}$$ eq A.8

The classical Hamiltonian for the vibrational motion in the harmonic approximation is thus

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$ eq A.9