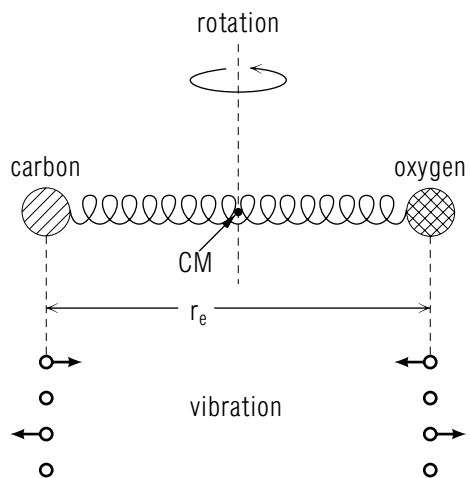


# DIATOMIC MOLECULES: PROPERTIES FROM ROTATION - VIBRATION SPECTRA



## DIATOMIC MOLECULES: PROPERTIES FROM ROTATION - VIBRATION SPECTRA

by  
Peter Signell  
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**Input Skills:**

1. Solve two simultaneous linear equations in two unknowns.
2. Given a set of energy levels, compute the wavelengths, frequencies, and energies of the photons involved in transitions among them (MISN-0-216).
3. Explain the origin of the classical rotational kinetic energy term:  $L^2/(2I)$  (MISN-0-251).
4. Explain each symbol in the quantum mechanical angular momentum expression:  $L^2 = \ell(\ell + 1)\hbar^2$  (MISN-0-251).
5. (Helpful) Explain the origin of the reduced mass  $\mu$  in the 2-body moment of inertia:  $I = \mu r^2$  (MISN-0-45).

**Output Skills (Knowledge):**

- K1. Define “wave number” in terms of frequency.
- K2. Draw diatomic molecule vibration-rotation energy levels, label them with quantum numbers, and indicate P-Branch and R-Branch allowed transitions.
- K3. Explain the origin of each term in the expression for the vibration-rotation energy levels of diatomic molecules.

**Output Skills (Problem Solving):**

- S1. Given the spectrum of a species of diatomic molecule and values for two of the wave numbers: (i) identify the transitions and sketch them on an energy level diagram; and (ii) determine the equilibrium separation of the atoms, their inter-atomic force constant, and their frequency of radial vibration.

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# DIATOMIC MOLECULES: PROPERTIES FROM ROTATION - VIBRATION SPECTRA

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## 1. Overview

**1a. Importance, Examples, Method, Results.** In a broad sense, molecular structure determines the form of everything we see in daily life. This includes the texture of our skin, the shapes of clouds, the hardness of wood, and the varying resiliencies of plastics. If we want to gain an understanding of the basis of these things, and in fact all of biology, chemistry, and materials science, we must understand something of molecular structure. In order to achieve a clear understanding of general principles, we usually begin by studying the simplest system available: here it is the diatomic molecule. Examples of two-atom molecules are:  $H_2$ ,  $O_2$ ,  $CO$ ,  $HCl$ ,  $BeF_1$ , etc. We will work through the general procedure for determining several properties of diatomic molecules from their spectra, then treat  $CO$  in detail as an example. Finally, we will interpret some aspects of daily life in terms of the results.

**1b. Diatomic Molecules Oscillate and Rotate.** The two atoms in a diatomic molecule, like  $CO$  in Fig. 1, can be thought of as being connected by a spring, so their motions are<sup>1</sup> simultaneously oscillations about their equilibrium radii from the CM point,<sup>2</sup> and rotation of the equilibrium points about a perpendicular axis through the CM. An observer far away from the molecule might see only the rotational motion. On the other hand, one rotating with the molecule would see only the synchronized in - and - out oscillations of the two atoms. Of course the rotational mode does not exist in a solid, but is continually excited and deexcited by molecular collisions in liquids and gases. In contrast, the oscillations can never cease, whether the molecule is in the solid, liquid or gaseous state.

<sup>1</sup>For a full discussion of why the inter-atomic force can be considered spring-like, see "Small Oscillations" (MISN-0-28).

<sup>2</sup>For a discussion of the CM (Center of Mass) see "Two-Body Kinematics and Dynamics" (MISN-0-45).

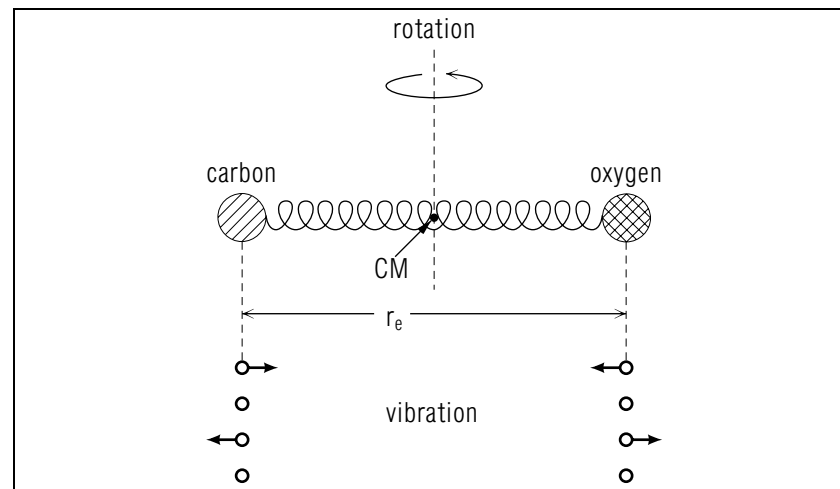


Figure 1. A representation of a  $CO$  molecule

### 1c. Spring Constant and Equilibrium Separation as Output.

A diatomic molecule's spectral - line frequencies are determined by its energy - level separations, and these in turn are determined by its spring - like force's stiffness  $k$  and equilibrium separation  $r_e$ , plus the two atomic masses. The latter, being element masses, are very well known in all cases so are used as input to the calculation of  $k$  and  $r_e$  from molecular spectra. Of course in order to use a specific molecule's spectral lines with the general energy level formula, one must identify the specific energy levels involved in the production of the lines. This involves examination of a complete section of the spectrum, along with a usable knowledge of the two rules which select the allowed transitions between rotation - vibration energy levels. The flow chart illustrated in Fig. 2, reiterates those elements necessary to determine the oscillator's  $k$  and  $r_e$ .

## 2. Vibration-Rotation Transitions

**2a. The Energy Level Formula, Quantum Numbers.** The general vibration - rotation energy - level formula for diatomic molecules is the sum of two terms, one for the vibrational energy, the other for the rotational energy:

$$E(v, \ell) = h\nu_0\left(v + \frac{1}{2}\right) + \frac{\hbar^2\ell(\ell + 1)}{2\mu r_e^2} \quad (1)$$

$$v = 0, 1, 2, \dots 2\pi\nu_0 \equiv \sqrt{k/\mu}$$

$$\ell = 0, 1, 2, \dots$$

If classical mechanics had been valid, the equation would have been:<sup>3</sup>

$$E = \frac{1}{2}k(r - r_e)^2 + \frac{L^2}{2\mu r_e^2}. \quad (2)$$

In Eq. (1) and eq. (2),  $\mu$  is the molecule's reduced mass<sup>3</sup> formed from the masses of each of its constituent atoms ( $m_A$ ,  $m_B$ ):

$$\mu \equiv \frac{m_A m_B}{m_A + m_B}. \quad (3)$$

Using the classical  $E$  of Eq. (2) in Quantum Mechanics' Schrödinger equation, one finds the allowed energies to be those specified in Eq. (1), with the vibrational and rotational quantum numbers,  $v$  and  $\ell$ , being restricted to zero and the positive integers.<sup>4</sup>

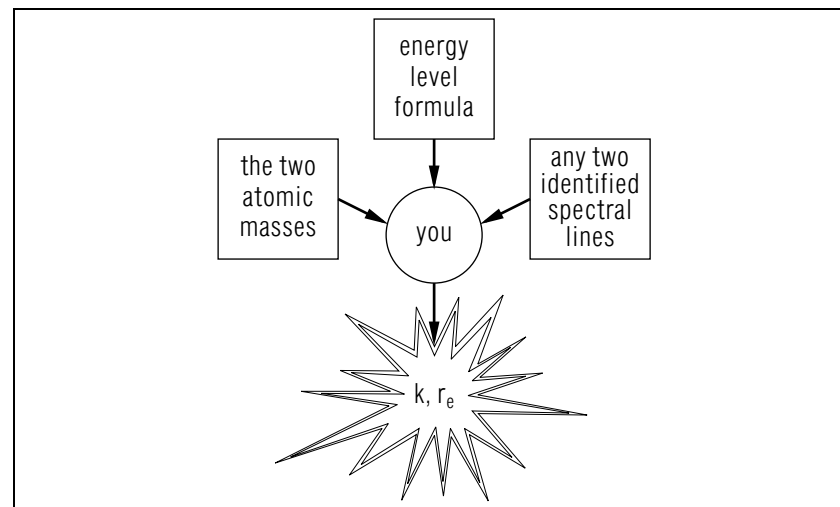
**2b. Energy Intervals: Rotational  $\ll$  Vibrational.** The energy-level separations corresponding to adjacent rotational  $\ell$ -values are generally about a thousandth of those corresponding to adjacent vibrational  $v$ -values:

Molecule	$\hbar^2/2I$ (ev)	$h\nu_0$ (ev)
H <sub>2</sub>	$.80 \times 10^{-2}$	0.54
O <sub>2</sub>	$.18 \times 10^{-3}$	0.19
CO	$.24 \times 10^{-3}$	0.27
HCl	$.13 \times 10^{-2}$	0.37

Of course this is merely a manifestation of the interatomic-force stiffnesses and equilibrium separations generally found in diatomic molecules. One might say that the values of the rather restricted range of free-oscillation frequencies,  $\nu_0$ , are due to rather stiff spring-like forces, or that the equilibrium separations  $r_e$  in the moment of inertia  $I$  are rather large *Help: [S-1]*.

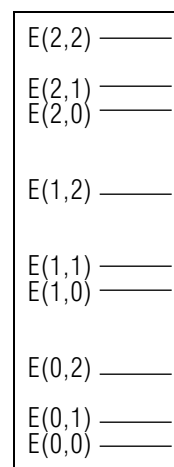
<sup>3</sup>See "Simple Harmonic Motion" (MISN-0-26) and "Two-Body Kinematics and Dynamics" (MISN-0-45).

<sup>4</sup>For the vibrational part of Eq. (1), see "The Schrödinger Equation in One Dimension" (MISN-0-242). For the rotational part, see "Quantization of Angular Momentum" (MISN-0-251).

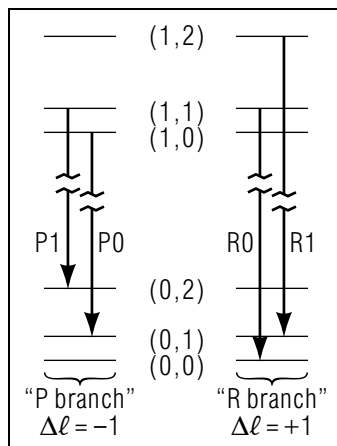


**Figure 2.** Tools to uncover the oscillator's physical properties

**2c. Energy Level Diagrams:  $E(v, \ell)$  Labels.** Since vibrational separation energies are very large compared to rotational, the energy level diagram consists of a number of groups of closely - spaced rotational levels separated by large vibrational gaps, as in Fig. 3 above (not to scale). The zero-rotation levels, those for which  $\ell = 0$ , are often called the vibrational energy levels: they are evenly spaced. The rotational levels are not.



**Figure 3.** A hypothetical energy level diagram illustrating the spacing between rotational and vibrational levels

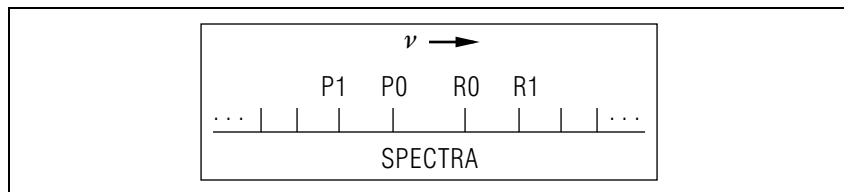


**Figure 4.** Energy level diagram depicting the vibrational and rotational energy levels for a hypothetical molecule.

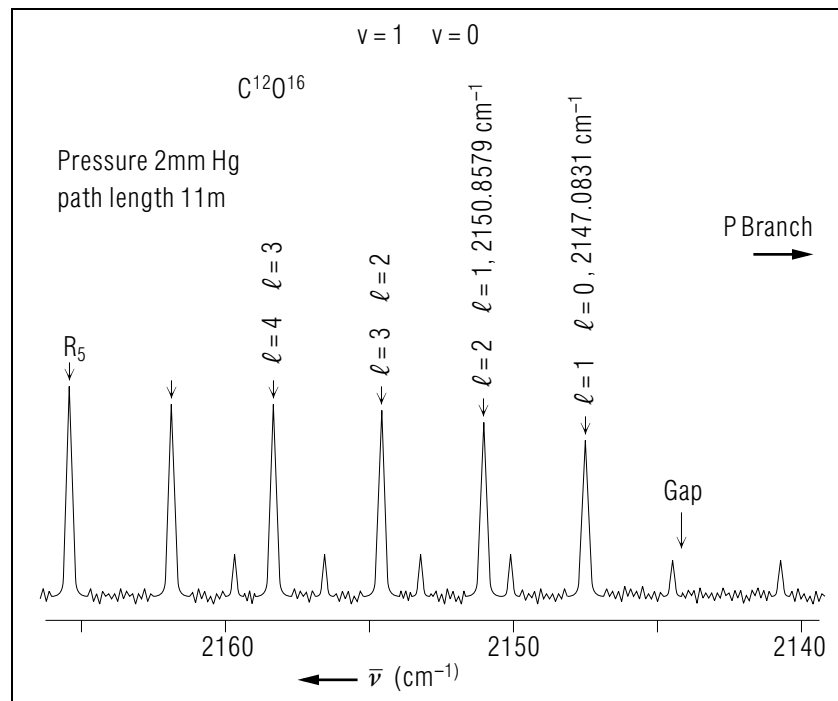
**2d. Transition Selection Rules for  $v$  and  $\ell$ .** Energy - level transitions involving the emission or absorption of light obey these selection rules:  $\Delta v = \pm 1$ ,  $\Delta \ell = \pm 1$ . This means that, for example,  $E(2, 1) \rightarrow E(1, 0)$  and  $E(2, 1) \rightarrow E(1, 2)$  are allowed but  $E(2, 1) \rightarrow E(1, 1)$  is forbidden. The  $\Delta \ell = \pm 1$  rule arises from the need of the photon to carry off  $1\hbar$  of angular momentum,<sup>5</sup> coupled with over - all conservation of angular momentum. The  $\Delta v = \pm 1$  rule comes from a higher level of Quantum Mechanics,<sup>5</sup> applied to oscillator transitions. Using these rules, the allowed transitions between the levels shown in Fig. 3 can be easily drawn in. Some of these transitions are illustrated in Fig. 4.

**2e. Spectra: The “P” and “R” Branches.** The vibration - rotation spectra are evenly spaced, but with a twice - as - wide gap at the center of each group as seen in Fig. 5. The part of the group at frequencies below the “missing” line is called the “P Branch” and it corresponds to

<sup>5</sup>For stimulated transitions: Perturbation Theory. For all transitions, stimulated or spontaneous: Quantum Electrodynamics. Transitions which violate the rule occur very infrequently compared to the rule-obeying transitions.



**Figure 5.** A typical vibrational-rotational spectrum.



**Figure 6.** The spectra of  $C^{12}O^{16}$  (see text)

frequencies for which  $\Delta \ell = -1$ . The higher frequency “R Branch” has  $\Delta \ell = +1$ . An easy way to identify the levels involved in any particular line then, is to find the central gap and count lines to the one you are interested in identifying.

### 3. C12-O16 as an Example

**3a. Input Data: Wave Numbers.** Suppose you have measured the  $v = 1 \leftrightarrow v = 0$  spectrum of  $C^{12}O^{16}$  and find, for the wave numbers  $\bar{\nu} \equiv \nu/c$ , the spectra depicted in Fig. 6 on the R Branch.<sup>6</sup> Note that frequencies increase to the left, wavelengths to the right. We will use two measured wave numbers;

$$\begin{aligned}\bar{\nu}_A &= 2147.0381 \text{ cm}^{-1}, \\ \bar{\nu}_B &= 2150.8579 \text{ cm}^{-1},\end{aligned}$$

<sup>6</sup>Figure from Rao, Humphries, Rank; Academic Press (1966)

the masses of  $C^{12}$  and  $O^{16}$ , the energy level formula, and the quantum numbers of the levels involved, to find  $k$  and  $r_e$ .

### 3b. Solution Steps.

- $I \equiv \mu r_e^2$ ; want  $r_e$ , can calculate  $\mu$ , get  $I$  from  $\bar{\nu}$ 's.  

$$\mu \equiv \frac{m_O m_C}{m_O + m_C} = 6.86 \text{ amu} = 6.39 \text{ GeV}/c^2$$

$$E_A = E(1, 1) - E(0, 0) = h\nu_0 + \hbar^2/I$$

$$E_B = E(1, 2) - E(0, 1) = h\nu_0 + 2\hbar^2/I \quad \text{Help: [S-2]}$$

$$\rightarrow I = \frac{\hbar^2}{E_B - E_A} = \frac{\hbar c}{2\pi c^2(\bar{\nu}_B - \bar{\nu}_A)} = 0.0822 \text{ nm}^2 \text{ GeV}/c^2$$

$$r_e = \sqrt{I/\mu} = 0.113 \text{ nm} \simeq 2 \text{ Bohr radii}$$
- $2\pi\nu_0 = \sqrt{k/\mu}$ ; want  $k$ , have  $\mu$ , get  $\nu_0$  from  $\bar{\nu}$ 's.  

$$k = \mu 4\pi^2 \nu_0^2 = (\mu c^2) 4\pi^2 (\nu_0/c)^2$$

$$\nu_0/c = (2E_A - E_B)/(hc) = 2\bar{\nu}_A - \bar{\nu}_B = 2.14 \times 10^5 \text{ m}^{-1}$$

$$\rightarrow k = 11.6 \text{ KeV nm}^{-2} = 10.6 \text{ lb/inch}$$

$$\nu_0 = 0.64 \text{ THz so the rotational period is 1.6 ps!}$$

Note: We have used the conversion factors:

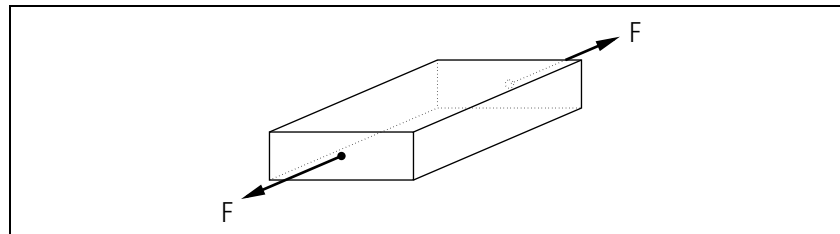
$$1 \text{ amu} = 0.931 \text{ GeV}/c^2$$

$$1 \text{ N} = 0.2248 \text{ lb}; 1 \text{ m} = 39.37 \text{ in.}$$

$$\text{and the constants: } \hbar c = 197.32 \text{ eV nm}; c = 300 \text{ Mm s}^{-1}$$

## 4. Interpretation of Results

**4a. Overview.** The equilibrium separation values found in diatomic molecules imply a rather large overlap of the atoms. This is a characteristic of very strong bonding. One can use the diatomic molecule's force constant to get a ball-park estimate of the macroscopic result of 3-dimensional bonds for real materials. For this purpose we can consider a solid to be connected of a 3-dimensional lattice of atoms, all connected by springs. We will imagine pulling on opposite ends of a slab of the material, stretching the springs. We will then compute the over-all force constant of the material from the force constants of each bond and the number of bonds involved.



**Figure 7.** A cube-like array of springs

**4b. The overall spring constant  $K$ .** If a cube-like array of springs is pulled apart by its ends as shown in Fig. 7, the over-all force constant  $K$  is related to the individual-spring force constants  $k$  by the relation:

$$K = N^{1/3} k$$

where  $N$  is the number of springs in the cube. The one-third power dependence arises from the  $(1/N^{1/3})$  series-coupling diminution of the force constant from the springs in the stretching direction, multiplied by the  $N^{2/3}$  parallel-coupling enhancement of the force constant from springs in the two dimensions perpendicular to the stretching direction. *Help: [S-3]*

**4c. Numerical Result and Comparison to Data.** The over all force constant for a 1 cubic inch array of diatomic-magnitude force constants  $k$  turns out to be about  $10^9$  lb/inch, to be compared to steel's value of  $3 \times 10^7$  lb/inch. The numbers which go into the calculation are:

$$N \simeq 10^{24} \text{ springs (bonds)}/\text{in}^3 (1.4 \times 10^{24} \text{ Fe atoms}/\text{in}^3 \text{ in steel})$$

$$k \simeq 10 \text{ lb/in.}$$

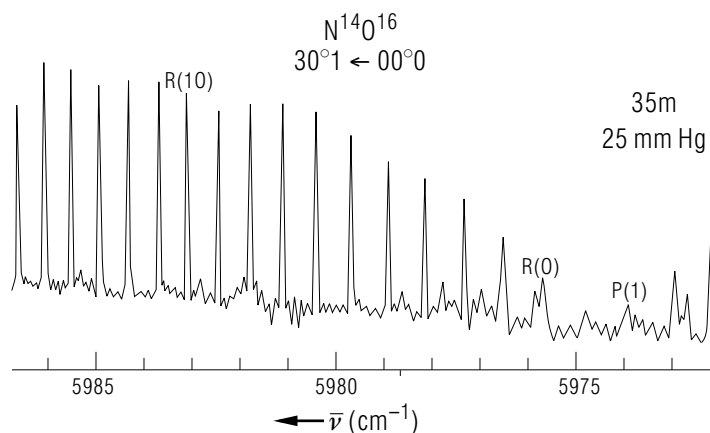
The result shows that diatomic molecule bonds are about 30 times stronger than the average bonds in steel.

## Acknowledgments

I wish to thank Paul Parker, Jack Hetherington, Brian Sharpee, and Harvey Edwards for helpful suggestions. Preparation of this module was supported in part by the National Science Foundation, Division of Science Education Development and Research, through Grant #SED 74-20088 to Michigan State University.

### PROBLEM SUPPLEMENT

1. Given the  $\nu = 1 \rightarrow \nu = 0$  vibration - rotation spectrum of nitrogen oxide ( $N^{14}O^{16}$ ) below:<sup>7</sup>



and the spectral lines:

$$\begin{aligned}\bar{\nu}_A &= 5978.7905 \text{ cm}^{-1} \\ \bar{\nu}_B &= 5978.0320 \text{ cm}^{-1},\end{aligned}$$

- Deduce the molecule's force constant, frequency of vibration, and equilibrium separation.
- Sketch the two transitions on an energy level diagram.

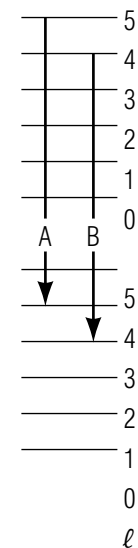
### Brief Answers:

- $$k = 4\pi^2 \mu c^2 (5\bar{\nu}_B - 4\bar{\nu}_A)^2 = 98.2 \text{ KeVnm}^{-2}$$

$$r_e = (hc)^{1/2} [2\pi(\bar{\nu}_A - \bar{\nu}_B)(\mu c^2)]^{-1/2} = 0.224 \text{ nm}$$

$$\nu_0 = c(5\bar{\nu}_B - 4\bar{\nu}_A) = 179 \text{ THz}$$

b.



<sup>7</sup>Rao, Humphries, Rank; Academic Press (1966)

## SPECIAL ASSISTANCE SUPPLEMENT

S-1 (from from Text Sect. 2b)

$h\nu_0 \gg \frac{\hbar^2}{2I}$  says the table.

then:  $\nu_0$  is large;

$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  so  $k$  is large,

or:  $I$  is large;

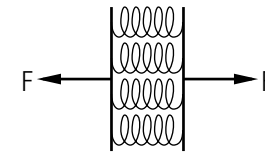
$I = \mu r_e^2$  so  $r_e$  is large.

S-2 (from Text Sect. 3b)

Following the directions in Sect. 2e, we look for a gap in the spectrum. We set the edge of a piece of paper along the spectra and mark the positions of the major lines. We then shift the paper to the right and find that a line is missing at the position marked "GAP". That demonstrates the gap's position.

S-3 (from Text Sect. 4b)

1. Parallel Springs: each spring has  $k$ , produces share of  $F$ :



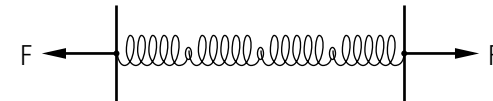
$$F = \sum_{i=1}^{n_{\parallel}} f_i = \sum_{i=1}^{n_{\parallel}} (-kx_i) = kxn_{\parallel}$$

where  $n_{\parallel} \equiv$  number of coupled parallel springs.

But:  $F \equiv -Kx$  defines the over-all force constant.

Hence:  $K = n_{\parallel}k$

2. Series Springs: each spring has  $k$ , force  $F$ :



$$F = f_i = -kx_i$$

$$x = \sum_{i=1}^{n_{\perp}} x_i = \sum_{i=1}^{n_{\perp}} \frac{F}{-k} = n_{\perp} \frac{F}{-k}$$

or:

$$F = -k \frac{x}{n_{\perp}}$$

where  $n_{\perp} \equiv$  number of coupled perpendicular springs.

Hence:  $K = \frac{k}{n_{\perp}}$

3. If there are  $N$  springs,

$$n_{\perp} = N^{2/3} \text{ (2 dimensions)}$$

$$n_{\parallel} = N^{1/3} \text{ (1 dimension)}$$

$$\text{total: } N = n_{\parallel}n_{\perp}$$



### MODEL EXAM

$$m_e = 0.51 \times 10^6 \text{ eV}/c^2; \quad \hbar c = 1.973 \times 10^{-7} \text{ eV m}$$

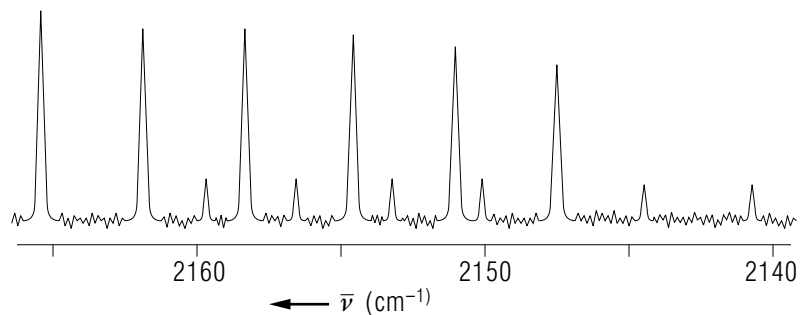
$$\hbar c = 1.2397 \times 10^{-6} \text{ eV m}; \quad c = 3 \times 10^8 \text{ m s}^{-1}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}; \quad 1 \text{ amu} = 0.931 \times 10^9 \text{ eV}/c^2$$

$$1 \text{ J} = 6.242 \times 10^{18} \text{ eV}$$

$$E(v, \ell) = (v + \frac{1}{2})\hbar\omega_0 + (\hbar^2/2I)\ell(\ell + 1)$$

1. See Output Skills K1-K3 in this modules *ID Sheet*.
2. Given the  $v = 1 \rightarrow v = 0$  vibration-rotation spectrum of carbon monoxide ( $\text{C}^{12}\text{O}^{16}$ ):<sup>8</sup>



and the spectral lines:

$$\bar{\nu}_A = 2158.4970 \text{ cm}^{-1},$$

$$\bar{\nu}_B = 2162.3173 \text{ cm}^{-1},$$

- a. Deduce the force constant  $k$  and the equilibrium separation  $r_e$  for the molecule.
- b. Sketch the two transitions on an energy level diagram.

<sup>8</sup>Rao, Humphries, Rank; Academic Press (1966)

