

# Workshop: Diatomic molecule vibrational and rotational spectra

## Quantum aspects of physical chemistry

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We have learned how the adiabatic and Born-Oppenheimer approximations allow us to separate the electronic, vibrational, rotational and center of mass contributions to the energy of a diatomic molecule. The key result is simple expressions for the electronic, vibrational and rotational contributions to the internal energy of the molecule. The purpose of this workshop is become familiar with these energy contributions and to see how to use them to understand vibrational and rotational spectra.

### ■ Internal energy components

Here is a summary of the expression for the components of the internal energy of a diatomic molecule in the adiabatic and Born-Oppenheimer approximations.

The internal energy,

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}},$$

is the sum of the electronic, vibrational and rotational contributions,

$$E_{\text{vib}} = \hbar \sqrt{\kappa/\mu} \left( i - \frac{1}{2} \right), \quad \kappa = \left( \frac{d^2 E_j(R)}{dR^2} \right)_{R=R_e}, \quad i = 1, 2, 3, \dots,$$

$$E_{\text{elec}} = E_j(R_e),$$

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}, \quad J = 0, 1, 2, \dots$$

These equations are a complete, approximate description of the quantum aspects of diatomic molecules. To test their correctness, the next step is to see how to use them to account for the structure and spectra of diatomic molecules.

### ■ Rotation of diatomic molecules

The rigid rotor approximation assumes that the molecule rotates at a fixed internuclear distance equal to the equilibrium bond length,  $R_e$ .

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}, \quad J = 0, 1, 2, \dots$$

The mass undergoing the rotational motion is the *reduced mass* of the molecule,

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

(I remember that the product of the masses goes in the numerator since the ratio must have units of mass.) To calculate the reduced mass for a given molecule AB we need to determine the mass of each atom, and to do this, we need to know which isotope of each atom is present in the molecule.

1. Recall that isotope masses are given in units of atomic mass,  $u$ . The atomic mass unit is defined such that the mass of exactly one gram of carbon 12 is Avogadro's number times  $u$ . Verify that this means that the atomic mass unit is  $1.66054 \times 10^{-27}$  kg.

2. Let's calculate the reduced mass for HCl. Since the energies pertain to a particular molecule, but because in a single molecule we have a particular isotope of each atom, we cannot use average molar masses. Assume that we have an HCl molecule consisting of the most stable isotope of each atom, namely  $^1\text{H}$  and  $^{35}\text{Cl}$ . The molar mass of  $^1\text{H}$  is 1.0078 and the molar mass of  $^{35}\text{Cl}$  is 34.9688. Show that the reduced mass of  $^1\text{H}^{35}\text{Cl}$  is  $1.62661 \times 10^{-27}$  kg.

3. The table below compares the reduced masses of  $^1\text{H}^{35}\text{Cl}$ ,  $^1\text{H}^1\text{H}$ , and  $^{35}\text{Cl}^{35}\text{Cl}$ . Explain, both mathematically and in terms of the rotational motion of the molecule, why the reduced mass of  $\text{Cl}_2$  is so different from that of HCl, and why the reduced mass of  $\text{H}_2$  is so much smaller than that of HCl. *Hint:* What is the reduced mass of the molecule AB, in the limit that an atom of B is infinitely heavier than an atom of A.

$^1\text{H}^{35}\text{Cl}$	$1.62661 \times 10^{-27}$ kg
$^1\text{H}^1\text{H}$	$8.36745 \times 10^{-28}$ kg
$^{35}\text{Cl}^{35}\text{Cl}$	$3.0691 \times 10^{-26}$ kg

Light can cause a molecule such as HCl to change its rotational state by the tug that the oscillating electric field of the light exerts on the dipole moment on the molecule. The result is that the rotational angular momentum can increase (absorption) or decrease (emission) by one unit,  $J \rightarrow J \pm 1$ .

4. Show that for absorption,  $J \rightarrow J + 1$ , the change of energy is

$$h\nu = \Delta E_{\text{rot}} = B_e 2(J + 1), \quad J = 0, 1, 2, \dots$$

in terms the equilibrium rotational constant defined as

$$B_e = \frac{\hbar^2}{2\mu R_e^2}.$$

At a certain temperature the molecules of gaseous  $^1\text{H}^{35}\text{Cl}$  can be in rotational states with  $J = 0, 1, \dots, 5$ .

5. Complete the table of the energies, in units of  $B_e$ , of the possible rotational absorption transitions.

J initial	J final	$\Delta E_{\text{rot}}$
0		
1		
2		
3		
4		
5		

6. Light of intensity  $I_0$  is passed through a gas of  $^1\text{H}^{35}\text{Cl}$ , and the intensity  $I$  of the light after it emerges from the gas is measured. Based on your table, sketch how the rotational absorption spectrum— $I/I_0$  versus light frequency—would look. What is the separation between the lines of the spectrum?

7. Show that for emission,  $J \rightarrow J - 1$ , the change of energy is

$$h\nu = -\Delta E_{\text{rot}} = B_e 2J, \quad J = 1, 2, 3, \dots$$

8. Complete the table of the energies, in units of  $B_e$ , of the possible rotational emission transitions.

J initial	J final	$-\Delta E_{\text{rot}}$
1		
2		
3		
4		
5		

9. A gas of  $^1\text{H}^{35}\text{Cl}$  is heated and the intensity of light emitted in rotational transitions is measured versus frequency. Based on your table, sketch how a plot of the rotational emission spectrum—intensity versus light frequency—would look. What is the separation between the lines of the spectrum?

Energies of rotational transitions are usually expressed as *wavenumbers*,  $\tilde{\nu} = 1/\lambda$  (note the "~" over the symbol  $\nu$ ). The conventional unit of wavenumber is  $\text{cm}^{-1}$ . The conversion factor from energy to wavenumber is  $(hc)^{-1}$ , and it is common refer to units in wavenumbers as a measure of energy. Thus, the energy of the  $^1\text{H}^{35}\text{Cl}$   $J = 0 \rightarrow J = 1$  absorption line is  $21.1874 \text{ cm}^{-1}$ .

10. What is the value of the  $^1\text{H}^{35}\text{Cl}$  rotational constant  $B_e$  in wavenumbers? The constant expressed in wavenumbers is written  $\tilde{B}_e$ , with "~" over the symbol  $B_e$ . Answer:  $10.5937 \text{ cm}^{-1}$ .

11. Show that the energy of the  $^1\text{H}^{35}\text{Cl}$   $J = 1 \rightarrow J = 2$  absorption line is  $42.3748 \text{ cm}^{-1}$ .

12. Calculate the energy, in  $\text{cm}^{-1}$ , of the  $^1\text{H}^{35}\text{Cl } J = 1 \rightarrow J = 0$  emission line. Answer:  $21.1874 \text{ cm}^{-1}$ .

The great importance of the rotational constant is that it is a "measure" of the bond distance.

13. Show that the equilibrium internuclear distance of  $^1\text{H}^{35}\text{Cl}$  is  $R_e = 1.27455 \text{ \AA}$ . *Hint:*  $B_e = h c \tilde{B}_e$ .

## ■ Vibration of diatomic molecules

The vibrational energy of a diatomic molecule in the harmonic oscillator approximation is

$$E_{\text{vib}} = h \nu_e \left( i - \frac{1}{2} \right), \quad i = 1, 2, 3, \dots,$$

in terms of the oscillator frequency  $\nu_e = (2\pi)^{-1} \sqrt{\kappa/\mu}$  and the force constant

$$\kappa = \left( \frac{d^2 E_j(R)}{dR^2} \right)_{R=R_e}.$$

Light can cause a molecule such as HCl to change its vibrational state if the dipole moment of the molecule changes as the molecule vibrates. In this case the vibrational quantum number can increase (absorption) or decrease (emission) by one unit,  $i \rightarrow i \pm 1$ .

14. Show that for the vibrational absorption,  $i \rightarrow i + 1$ , the change of energy (in wavenumbers) is

$$\tilde{\nu} = \frac{\Delta E_{\text{vib}}}{h c} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} = \tilde{\nu}_e$$

15. Show that for the vibrational emission,  $i \rightarrow i - 1$ , the change of energy is

$$\tilde{\nu} = -\frac{\Delta E_{\text{vib}}}{h c} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} = \tilde{\nu}_e$$

16. From these results, what do you expect the vibrational absorption spectrum of a molecule such as HCl to look like, versus light frequency? *Hint:* How would the spectrum change if temperature is changed?

The great importance of the vibrational constant is that it is a "measure" of the strength of the bond.

17. Assume that the energy of the  $^1\text{H}^{35}\text{Cl } i = 1 \rightarrow i = 2$  vibrational absorption line is  $2885.31 \text{ cm}^{-1}$ . Show that the value of the force constant is  $\kappa = 480.474 \text{ kg s}^{-2}$ .

18. Explain whether the dissociation energy of  $^1\text{H}^{35}\text{Cl}$  can be estimated in the harmonic oscillator approximation.

Real molecules dissociate and so we know that far from the equilibrium position the higher order, so-called *anharmonic terms* in the Taylor series expansion of the electronic energy,  $E_j(R)$ , can no longer be neglected.

19. Explain why in real molecules the separation between vibrational energy levels must decrease with increasing vibrational quantum number  $i$ .

An approximate way to account for the decrease in energy level spacing is to view the harmonic oscillator energy expression,  $E_{\text{vib}} = h \nu_e (i - 1/2)$ , as the first term in an expansion in powers of  $i - 1/2$ . Adding the next terms gives

$$E_{\text{vib}} = h \nu_e (i - 1/2) - h x_e \nu_e (i - 1/2)^2$$

The dimensionless quantity  $x_e$  is known as the *anharmonicity constant*. The negative sign takes account of the decrease in separation between successive energy levels.

20. Show that the separation between adjacent energy levels in wavenumbers is  $\Delta E_{i,i+1} / (h c) = \tilde{\nu}_e - 2 i x_e \tilde{\nu}_e$ .

21. The energy of the  $^1\text{H}^{35}\text{Cl}$   $i = 2 \rightarrow i = 3$  vibrational absorption line in wavenumbers is  $2779.67 \text{ cm}^{-1}$ . Show that  $\tilde{\nu}_e = 2990.9476 \text{ cm}^{-1}$  and  $x_e \tilde{\nu}_e = 52.8186 \text{ cm}^{-1}$ . *Hint:* In determining the force constant earlier, we assumed the  $i = 1 \rightarrow i = 2$  transition energy was  $\tilde{\nu}_e$ , but in fact it is  $\tilde{\nu}_e - 2 x_e \tilde{\nu}_e$ .

A way to estimate the dissociation energy of a diatomic molecule is to determine the value of the vibrational quantum number,  $i_{\text{max}}$ , at which the vibrational energy stops increasing. This is the maximum possible value of the vibrational quantum number  $i$  in the anharmonic approximation.

22. Show that  $i_{\text{max}} = (\tilde{\nu}_e + x_e \tilde{\nu}_e) / (2 x_e \tilde{\nu}_e)$ .

23. Show that the maximum possible value of the vibrational quantum number in this anharmonic approximation to  $^1\text{H}^{35}\text{Cl}$  is  $i_{\text{max}} = 28.8$ .

Whether we round the value down or up is determined by which rounding will give the *highest* energy value.

24. Show that using  $i_{\text{max}} = 28$  the dissociation energy of  $^1\text{H}^{35}\text{Cl}$  is  $42307 \text{ cm}^{-1}$  while using  $i_{\text{max}} = 29$  the dissociation energy of  $^1\text{H}^{35}\text{Cl}$  is  $42340 \text{ cm}^{-1}$ . Based on these results, the estimated dissociation energy is  $\tilde{D}_e = 42340 \text{ cm}^{-1}$ .

The measured dissociation energy of  $^1\text{H}^{35}\text{Cl}$  is  $53194 \text{ cm}^{-1}$ . So the simple anharmonic approximation, and the measurement of the energies of two vibrational absorption lines has allowed us to estimate the dissociation energy to within 20%. In this way we see that vibrational frequency and anharmonicity together are a "measure" of the bond strength.