

# Chapter 4

## Molecules

Created in collaboration with Tee Kai Ze, Guan Xin, Jensie Low and Seow Ryan

### **Learning objectives**

By the end of this chapter, you should be familiar with some concepts of molecular spectroscopy. You will be introduced to techniques and methods used to locate, identify molecules based on their fingerprints, and how molecules are identified in space. Finally, you will have the opportunity to explore recent datasets of astrochemistry research.

### **Learning flow**

Before week 5 lecture, do the pre-lecture homework and briefly read through the lecture notes.

During week 5 lecture, we will go through most of the content in this chapter. As usual, some activities will be incorporated to break the monotony. If we run out of time, part of the content may be discussed in week 6 lecture.

In week 6 IS, we will discuss the questions at the end of the chapter.

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## 4.1 Pre-Lecture Homework

### 4.1.1 Boltzmann Distribution

Even before we had the statistical interpretation of quantum mechanics, statistics was applied to fundamental science to account for observations. Ludwig Boltzmann and other founders of statistical mechanics used methods of probability theory to bridge the microscopic world and macroscopic observations such as temperature, work, heat and chemical processes.

Say we have a macroscopic system at some temperature  $T$ . Suppose there exists a variety of possible “states” (state 1, state 2, etc), each with its characteristic energy ( $E_1, E_2$ , etc.). The probability of occurrence of a state is related to the state’s energy via the Boltzmann distribution:

$$\text{Probability of state } i \text{ occurring} = p_i \propto e^{-E_i/kT} \quad (4.1)$$

where  $k = 1.38 \times 10^{23} \text{ JK}^{-1}$  is the Boltzmann constant.

Have you heard of the phrase “particles prefer lower energy states”? Explain this using Boltzmann distribution.

In the atomic spectrum experiment (hope that you have started doing it!), you will see that the intensities of each spectral line is different. Boltzmann distribution partly explains this. How?

Read up more on Boltzmann distribution and find examples of how it is used in other fields.

#### 4.1.2 Clouds in outer space

The space between stars is not empty. It is dotted with matter, at some places denser than others. As they exist in the regions between and around stars, they are known as the interstellar medium (ISM). The ISM can be made of clouds of hydrogen and helium gas, as well as “dust grains” that contain heavier elements. Interactions between matter and light within the ISM give rise to beautiful astronomical objects called nebulae.



Figure 4.1: Left: Emission nebulae Heart (IC 1805) and Soul (IC 1845) nebulae. Center: Witch Head nebula (IC 2118), a reflection nebula. Right: Snake nebula (B 72), a dark nebula. All images are from apod.nasa.gov

Why is an emission nebula reddish in colour, and a dark nebula dark?

## 4.2 Classical Rotations and Vibrations

### 4.2.1 Rigid Rotor

Consider a particle of mass  $m$  rotating around an axis. The inertia towards linear motion is the particle's mass  $m$ . For rotational motion, mass is insufficient to quantify the amount of inertia for rotational motion. The distance away from the axis of rotation plays a role too. One way to demonstrate this is to rotate a rod with a weight attached. The further the weight is away from the axis of rotation, the harder it is to rotate. The reluctance to rotate is termed as moment of inertia.

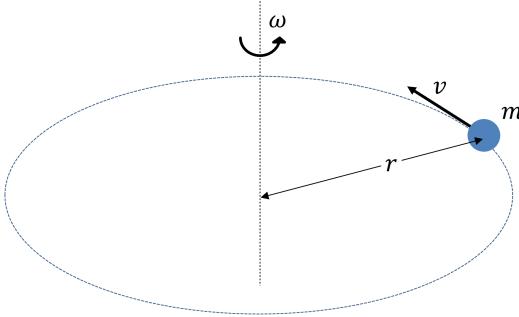


Figure 4.2: A particle with mass  $m$  rotating about an axis at a distance  $r$  away, moving with (instantaneous) linear speed  $v$  and angular speed  $\omega$ . The particle possess a moment of inertia  $I = mr^2$  and an angular momentum of  $L = I\omega$ .

The particle's motion is characterised by:

- $r$  : distance between the particle and axis
- $I$  : moment of inertia
- $v$  : velocity
- $\omega$  : angular velocity
- $p$  : linear momentum
- $L$  : angular momentum
- $T$  : kinetic energy

The above parameters are closely related by the following equations:

$$I = mr^2 \quad (4.2)$$

$$v = r\omega \quad (4.3)$$

$$p = mv \quad (4.4)$$

$$L = I\omega \quad (4.5)$$

$$T = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2 \quad (4.6)$$

Ex. Spend some time with the above equations and make sense of the ones that involve angular motion.

Let us now consider the case of two particles with masses  $m_1$  and  $m_2$  joined by a rigid (massless) rod of length  $R$ . The 2-body system has a center of mass. Let us set the center of mass to be at the origin, mass  $m_1$  to be located at distance  $r_1$  away from the center of mass, and mass  $m_2$  at  $r_2$  away. Since the 2 masses are at opposite sides of the center of mass,

$$r_1 + r_2 = R \quad (4.7)$$

By principle of moments<sup>1</sup>

$$m_1 r_1 = m_2 r_2 \quad (4.8)$$

Now set these masses on the  $xy$  plane, have the  $z$  axis to cut through the center of mass and allow the masses to rotate around the  $z$  axis. This is the rigid rotor which we will use to model a rotating diatomic molecule.

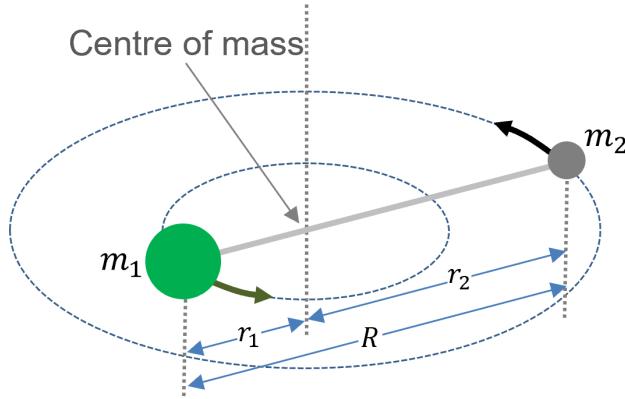


Figure 4.3: Two particles with masses  $m_1$  and  $m_2$  joined by a rigid massless rod rotates about an axis that cuts through the centre of mass.

Ex. Use Eqs.(4.7) and (4.8) to derive

$$r_1 = \frac{m_2}{m_1 + m_2} R \quad (4.9)$$

$$r_2 = \frac{m_1}{m_1 + m_2} R \quad (4.10)$$

The moment of inertia of the system is given by

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_1 \left( \frac{m_2}{m_1 + m_2} R \right)^2 + m_2 \left( \frac{m_1}{m_1 + m_2} R \right)^2 \\ &= \frac{m_1 m_2 R^2}{(m_1 + m_2)^2} (m_2 + m_1) \\ &= \frac{m_1 m_2}{m_1 + m_2} R^2 \\ &= \mu R^2 \end{aligned} \quad (4.11)$$

<sup>1</sup>CW moments = CCW moments, which you have learned in Sec school!

$\mu$  is called “effective mass”. By expressing the moment of inertia in Eq.(4.11) allows us to treat the 2-body system like a single particle.

Since the rotor is “rigid”, the two masses share the same angular velocity  $\omega$ . The angular momentum of the system is

$$L = I\omega \quad (4.12)$$

The kinetic energy is

$$T = \frac{1}{2}m_1r_1^2\omega^2 + \frac{1}{2}m_2r_2^2\omega^2 = \frac{1}{2}I\omega^2 = \frac{L^2}{2I} \quad (4.13)$$

What is the potential energy of the system?

$$V = 0 \quad (4.14)$$

No potential energy, the rigid rotor here rotates “freely”.

### 4.2.2 Harmonic Oscillator

In chapter 2, we learned about the case of one particle attached to a massless spring. We shall now extend the idea to two particles connected by a spring.

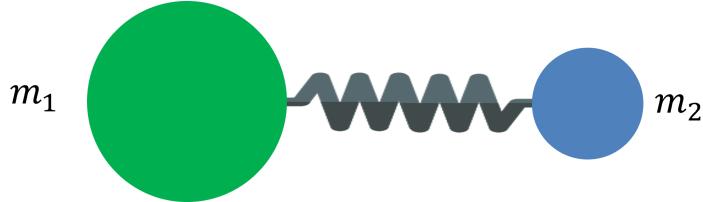


Figure 4.4: Two particles with masses  $m_1$  and  $m_2$  joined by a massless spring.

The equations of motion of the two masses are

$$m_1\ddot{x}_1 = k(x_2 - x_1 - x_0) \quad (4.15)$$

$$m_2\ddot{x}_2 = -k(x_2 - x_1 - x_0) \quad (4.16)$$

Similar to how the 2-masses rigid rotor can be re-modeled as a rotation of a particle with an effective mass, the 2-masses-connected-by-a-spring system can be re-modeled as a single particle undergoing simple harmonic motion:

$$\ddot{x} = -\omega^2 x \quad (4.17)$$

where  $\omega$  is the angular frequency

$$\omega = \sqrt{\frac{k}{\mu}} \quad (4.18)$$

$k$  is the spring constant, and  $\mu$  is the effective mass given by

$$\mu = \frac{m_1m_2}{m_1 + m_2} \quad (4.19)$$

The kinetic energy of the system is

$$T = \frac{1}{2}\mu\dot{x}^2 = \frac{p^2}{2\mu} \quad (4.20)$$

The potential energy of the system is

$$V = \frac{1}{2}kx^2 = \frac{1}{2}\mu\omega^2x^2 \quad (4.21)$$

For the interested reader, the detailed derivation of the above equations is given in Appendix.

### 4.3 The Quantum Molecule

In the previous chapter, we have established what is a chemical bond and how electron transitions between energy levels of a molecule are observable. Building upon the principles of linear combination of atomic orbitals, one might expect discrete energy levels and transitions leading to discrete peaks in molecular spectra. Is it really so?

Let us take a look at a molecule you should see and eat everyday: chlorophyll :) There are 2 types of chlorophyll (Chl), Chl a and Chl b. Their molecular structure and (solvent-free) absorption spectra are shown in the figure below.

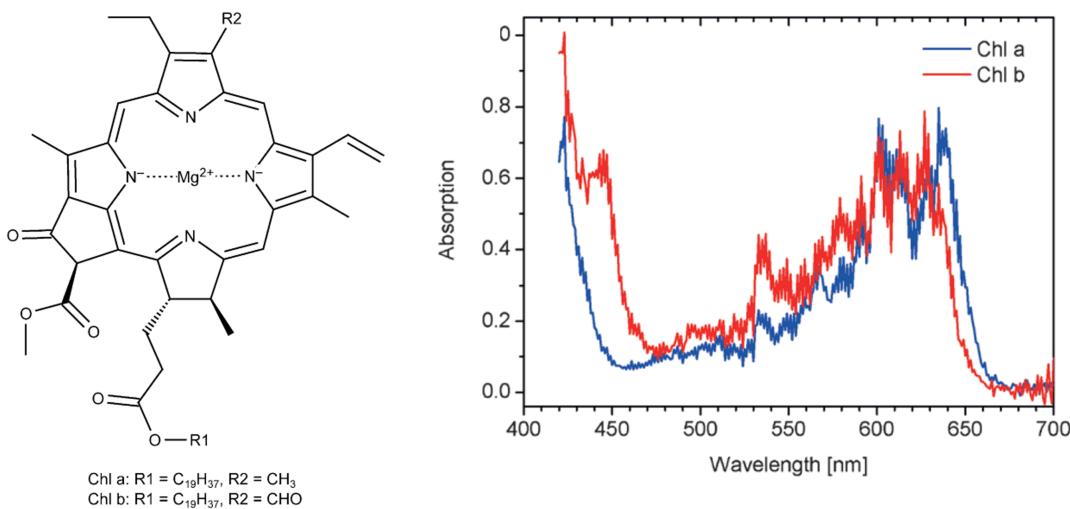


Figure 4.5: Left: Structure of Chlorophyll (Chl) a and b. Right: Absorption of Chl a and b taken using a solvent free (gas phase) technique. Adapted from Milne, B. F., Toker, Y., Rubio, A., Nielsen, S. B. Unraveling the Intrinsic Color of Chlorophyll. *Angew. Chem. Int. Ed.* **2015**, 54, 2170

**Ex. From the spectrum above, explain why leaves are green.**

One notable difference between atomic and molecular (UV-Vis) spectra is that while the former is composed of distinct discrete peaks, the latter usually exhibit broader peaks or bands. A fine example of a molecular spectrum is that of Chl a and b shown above. What is the reason for the broader bands as opposed to narrow peaks?

One major contributing factor to the broad bands is the existence of vibrational and rotational energy levels within an (molecular) electronic state. For a molecule at a certain electronic orbital state, it can wobble and rotate. The vibrations and rotations changes the energy of the molecule slightly. As many vibrational and rotational states are possible for each molecular orbital state, the electronic state no longer possesses a single well-defined discrete energy but a range of energies. Depending on the resolution of the spectrometer used, the band of energy may be resolved such that the finer structures can be seen (see spectrum of Chl a and b above). Very often a lower resolution spectrometer is used to probe the molecule , in which case the finer details will smear out to give smooth and broad peaks (google image for chlorophyll spectrum).

The energies associated with transitions across electronic energy states are orders of magnitude larger than that of the vibrational states, which are in turn orders of magnitude larger than transitions across rotational states.

$$\Delta E_{MO} \approx 10^3 \Delta E_{vib} \approx 10^6 \Delta E_{rot} \quad (4.22)$$

A simplistic representation of this is given in the following diagram:

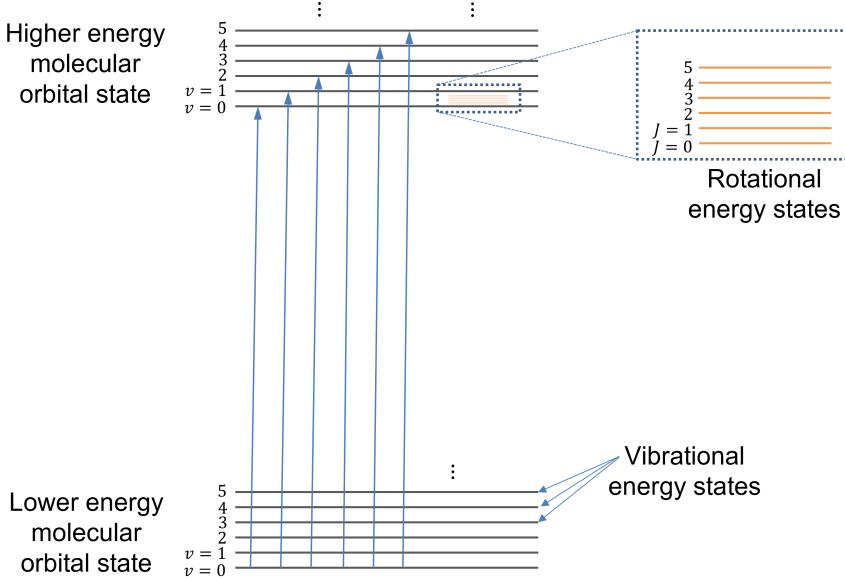


Figure 4.6: Energy states of a molecule i much richer than that of an atom. The allowed vibrational and rotational motion contributes to finely distributed energy levels within each electronic molecular orbital state.

In order to simplify the quantum description of the molecule, Born and Oppenheimer assumed that the motion of the electrons and nuclei in molecules can be considered separately. Since the mass of the nuclei is of several orders of magnitude heavier than the electrons, the motion of nuclei is negligible to that of the electrons. The energies of the electron can then be calculated at fixed internuclei distances. **The energies of electronic, vibrational and rotational states can be considered to be independent of each other.** This is known as the Born-Oppenheimer approximation.

In this course we will examine the vibrational and rotational energy levels and their corresponding transitions in greater details.

### 4.3.1 Rotational Energy Levels and Microwave Spectroscopy

Let us consider the rotation of a diatomic molecule. We assume the bond between the two atoms is rigid, meaning that the internuclear distance does not change. As shown in section 4.2.1, the kinetic and potential energies of the system is

$$T = \frac{L^2}{2I} \quad (4.23)$$

and

$$V = 0 \quad (4.24)$$

respectively. The Schrödinger equation is

$$-\frac{\hbar^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \theta^2} \right] \psi = E\psi \quad (4.25)$$

It is out of the scope of the course to derive Eq.(4.25). For the interested reader, see the Appendix on a note about operators.

The procedure to solve the above SE is in essence similar to how it was done in Chapter 3. The allowed energies of the system are

$$E = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \quad (4.26)$$

where  $J = 0, 1, 2, 3, \dots$  is the rotational quantum number and  $B = \hbar^2/2I$  is called the rotational constant.

The rotational constant depends on the moment of inertia of the diatomic system, which in turn depends on the masses of the nuclei as well as the bond length. Different molecules will have different rotational constants thus making the set of rotational energies unique to each molecule.

The rotational constant above has units of energy. Some (eg. radio astronomers) like to state the rotational constant in units of frequency (Hz). In this case, divide the above  $B$  by  $h$ . Other (eg. chemists) prefer to state the rotational constant in units of wavenumber ( $\text{cm}^{-1}$ ). In this case divide the above by  $hc$  where  $c = 3.00 \times 10^{10} \text{ cm s}^{-1}$  is the speed of light.

Define  $P(J)$  as the probability of a molecule being in the  $J^{\text{th}}$  energy state, we have

$$P(J) = (2J+1)P(0) \exp\left(-\frac{BJ(J+1)}{kT}\right) \quad (4.27)$$

where  $P(0)$  is the probability of finding the particle at ground state ( $J = 0$ ).

The diatomic molecule with a permanent dipole moment can transit from one rotational energy state to another by absorbing or emitting a photon.<sup>2</sup> By examining the probability of transitions, it can be shown that only transitions across more than one energy level is highly improbable. Thus transitions across rotational energy levels are restricted to the following selection rule

$$\Delta J = \pm 1 \quad (4.28)$$

This means that transitions such as  $J = 3 \rightarrow 2$  and  $J = 3 \rightarrow 4$  are allowed while  $J = 5 \rightarrow 3$  is highly unlikely.

The energy of a photon emitted in a  $J + 1 \rightarrow J$  transition is given by

$$\begin{aligned} hf &= \Delta E = B(J+1)(J+2) - BJ(J+1) \\ hf &= 2B(J+1) \end{aligned} \quad (4.29)$$

The probability of particle residing in the  $J^{\text{th}}$  energy state given in Eq.(4.27) gives the relative intensity of the spectral line.

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Ex. Show that the rotational spectrum of a diatomic molecule is a set of equally spaced spectral lines with separation  $2B$ .

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Ex. Suppose you are given the rotational spectrum of a molecule, how does one find the internuclear distance of the molecule?

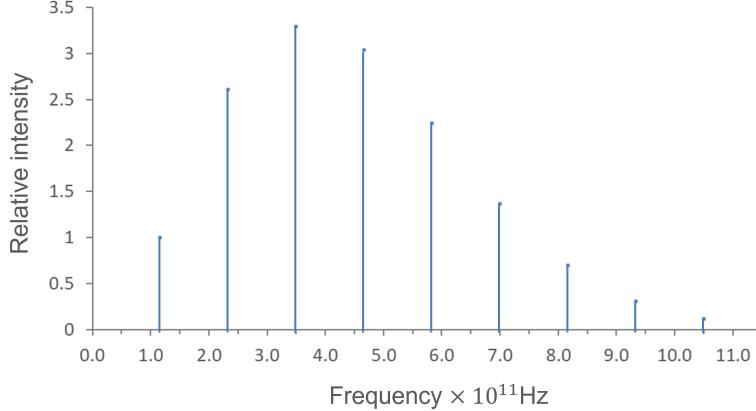
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<sup>2</sup>Homonucleus diatomic molecules such as  $\text{H}_2$  and  $\text{N}_2$  do not have a permanent dipole moment and cannot undergo light-induced rotational transitions.

Ex. The figure below is the rotation spectrum of CO. Explain qualitatively why different spectral lines have different intensities.



### 4.3.2 Ro-Vibrational Energy Levels and IR Spectroscopy

In the previous section, the bond between atoms are treated as a rigid rod. In this section, we shall allow the bonds to stretch and compress. This means that the molecule can vibrate when the atoms are displaced from their equilibrium position.

Let us consider the case of a diatomic molecule. We model its vibrational motion with a harmonic oscillator described in section 4.2.2, i.e. a 1D system with effective mass (see Eq.(4.19))

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (4.30)$$

where  $m_1$  and  $m_2$  are the masses of the atoms. The potential energy is (see Eq.(4.21))

$$V = \frac{1}{2} \mu \omega^2 x^2 \quad (4.31)$$

The Schrödinger equation is

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 \psi = E\psi \quad (4.32)$$

and the boundary conditions are

$$x \rightarrow \pm\infty, \psi(x) \rightarrow 0 \quad (4.33)$$

Without going into the details of solving the quantum mechanics for a harmonic oscillator, we just state here the results. The molecules display discrete vibrational energy states given by

$$E = \hbar\omega \left( v + \frac{1}{2} \right), \quad v = 0, 1, 2, 3, \dots \quad (4.34)$$

where  $v$  is the vibrational quantum number which takes on integer values.

For transitions across vibrational energy levels, a similar rule to rotational levels holds:

$$\Delta v = \pm 1 \quad (4.35)$$

This means that all allowed transitions across vibrational energy levels will have energy

$$\Delta E_{\text{vib}} = E_{v+1} - E_v = \frac{\hbar\omega}{2\pi} \left( \left( v + 1 + \frac{1}{2} \right) - \left( v + \frac{1}{2} \right) \right) = \frac{\hbar\omega}{2\pi} \quad (4.36)$$

Note the the lowest energy state is non-zero.

**Ex.** The fundamental oscillator (angular) frequency  $\omega$  of  $\text{H}^{35}\text{Cl}$  is  $5.44 \times 10^{14}\text{Hz}$ .

- (a) Find  $\Delta E_{\text{vib}}$  and the corresponding wavelength of transition.
- (b) In what category of the EM spectrum does this transition belong? (radio/microwave/IR/visible/UV/X-ray)
- (c) Compare the energy of vibrational transitions of HCl to one of its rotational energy level transitions (say  $J = 2 \rightarrow 1$ ).
- (d) Chemist usually report vibrational spectroscopy results in units of wavenumber ( $\text{cm}^{-1}$ ). Convert your answer in part (a) to wavenumber and compare it to values you can find in the literature.

Although it seems from Eq.(4.36) that the vibrational spectrum is a simple single line for a molecule, it is not so after taking rotational energies into account. In each vibrational energy *band*, the molecule can be at many different rotational energy states. For a heterogenous diatomic molecule, a transition across the vibrational energy will be accompanied by a change in rotational levels with the following rule:

$$\Delta v = \pm 1, \Delta J = \pm 1 \quad (4.37)$$

The vibrational spectrum of a molecule thus exhibits 2 bands. The higher energy band (R-branch) comprises of  $\Delta J = +1$  transitions, while the lower energy band (P-branch) comprises of  $\Delta J = -1$ .

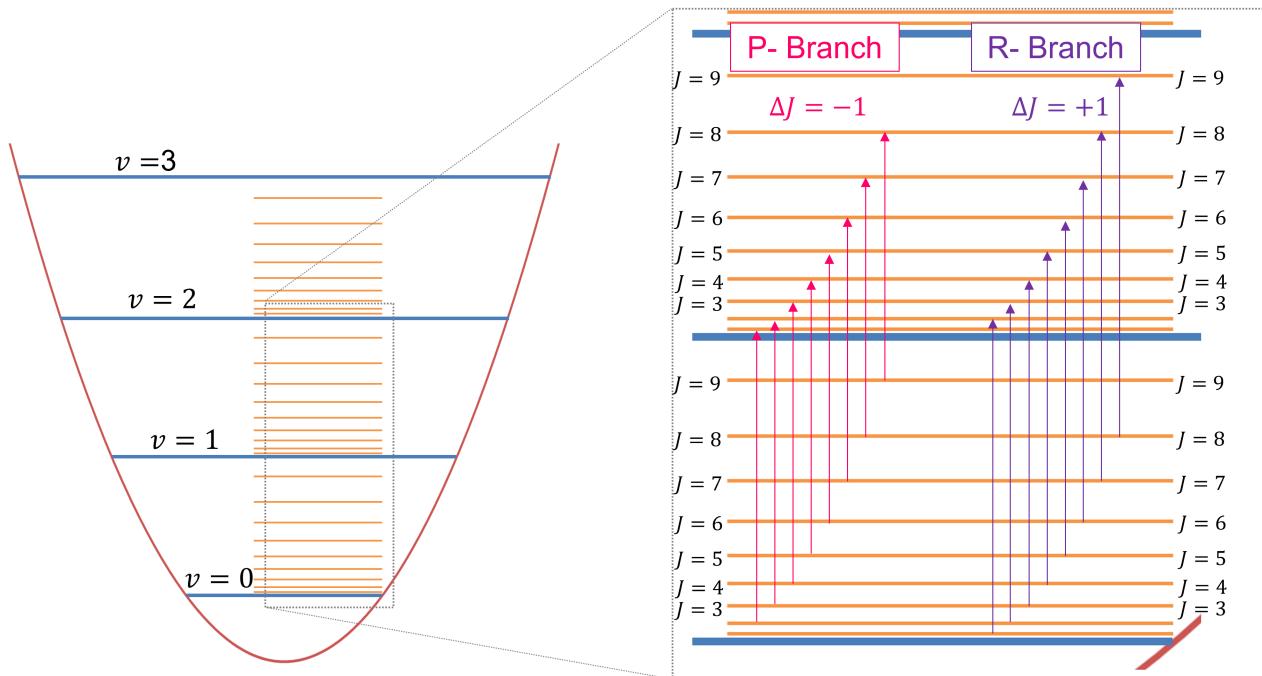


Figure 4.7: Schematic of vibrational and rotational energy levels with P- and R-branch ro-vibrational transitions.

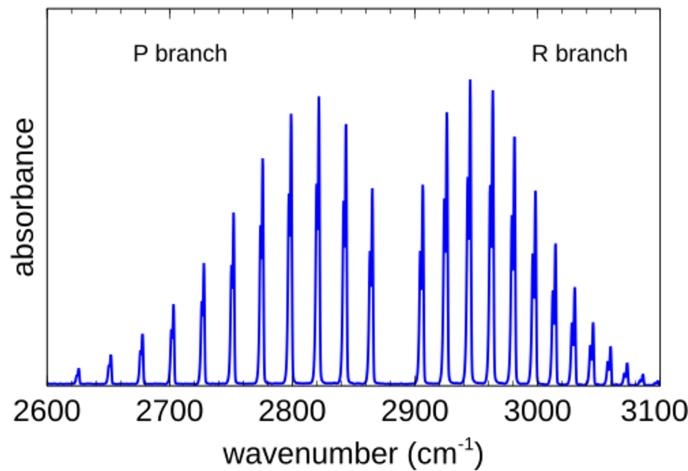


Figure 4.8: Ro-vibrational spectrum of HCl. Image credit: Cnrowley CC-SA-4.0-BY

The image above is a ro-vibrational absorbance spectrum for HCl, and we can clearly see that there is a peak near the centre that is missing. That missing peak belongs to the pure vibrational transition,  $\Delta E = \frac{1}{2}\hbar\omega$ . To the left, is the P branch (as in P for poor), where  $\Delta J = -1$ , and to the right is the R branch (as in R for rich), where  $\Delta J = +1$ . The pure vibrational ( $\Delta J = 0$ ) peak do not show up as the transition is much less favourable than the  $\Delta J = \pm 1$  transitions.

Ex. Examine the ro-vibrational spectrum of HCl in the above figure closely. Try to explain the features you see.

## 4.4 Molecules in space

### Interstellar Reddening

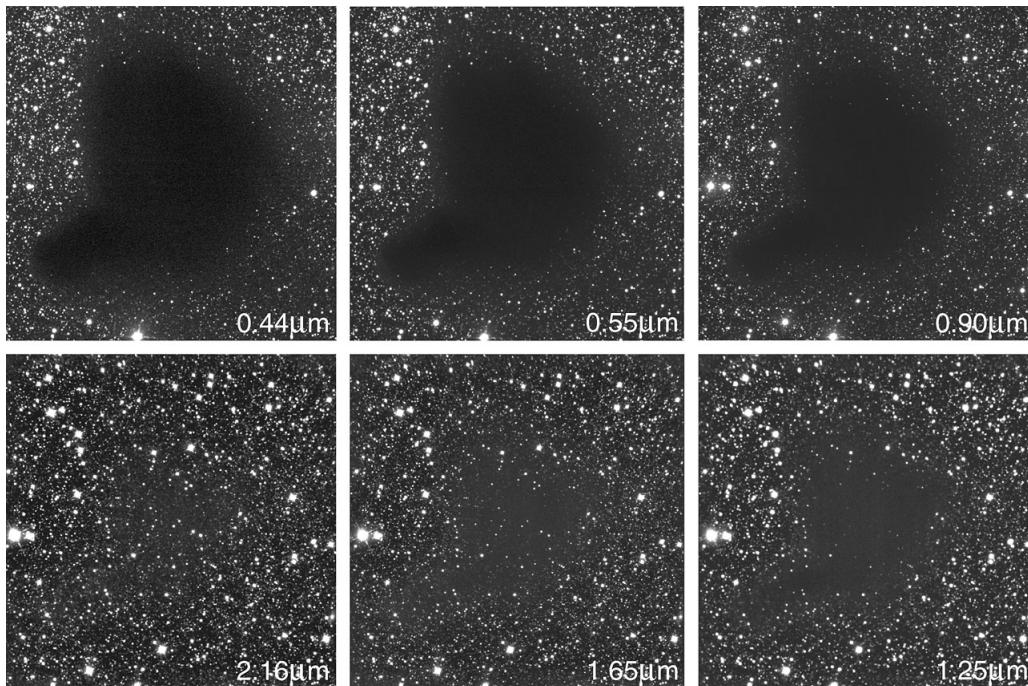


Figure 4.9: The dark nebula B68 viewed with different wavelengths of light. Image from [www.eso.org](http://www.eso.org)

Stars behind the dark molecular cloud B68 could not be seen at optical wavelengths, but reveal themselves when viewed with infra-red light optics and detectors. This also means that when viewed over an extended broadband spectrum, the light from behind the cloud will look redder than it actually is. This is known as interstellar reddening, and B68 presents a pretty extreme case of it.

What is interstellar reddening in general? When we learned about diffraction of light, we saw that red light diffracts less than green or blue light. Such wavelength dependence is generally exhibited when the size of the object in the path of the light is comparable to the wavelength of the light. When light **scatters** off small particles, red light is less affected and are able to transmit more easily through a region of gas than its shorter wavelength counterparts. This is the reason why the sun looks red when it is low on the horizon at dawn or dusk. Conversely, blue or shorter wavelength light scatters more and this is the reason why the sky is blue!

With the use of telescopes that see in infra-red light, we can peer *through* the dense cloud of B68. But what if we want to know what is inside the cloud itself? Take a spectrum! Or equivalently in the context of radio astronomy, view the cloud at wavelengths corresponding to molecular transition!

### Identification of molecules

Recall that molecules have rotational energy levels, and transitions between these levels absorb or emit wavelengths in the microwave/radiowave regime. In the interstellar medium (ISM) where temperature is cold, these low energy transitions can take place quite frequently. Taking a spectrum or viewing the ISM at these wavelengths reveal a wealth of chemical species.

Ex. See the spectrum and table below. Try to identify some of the chemical species in TMC-1.

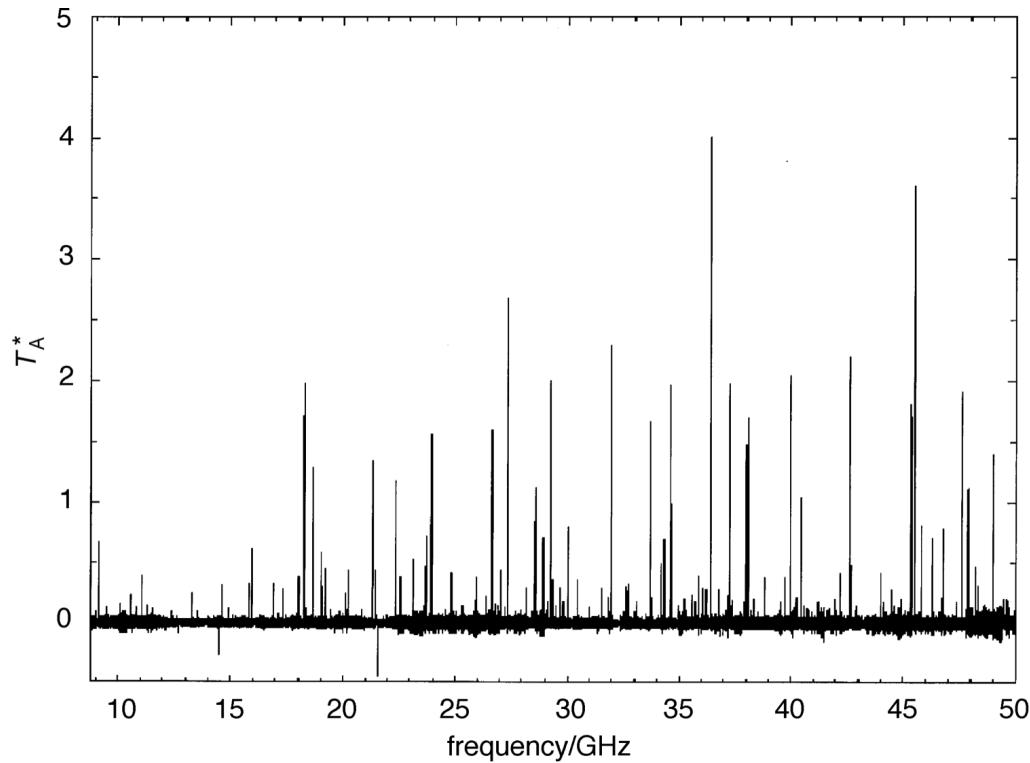


Figure 4.10: Spectrum toward TMC-1. Taken from M. Ohishi, N. Kaifu, Faraday Discuss, 109, 205 (1998)

Table 1. Parameters of Example Linear Molecules in  ${}^1\Sigma$  States

Molecule	Name	B (GHz)	$\mu$ (D) <sup>a</sup>	Molecule	Name	B (GHz)	$\mu$ (D) <sup>a</sup>
CO	Carbon Monoxide	57.635968	0.11011	CS	Carbon Monosulfide	24.495562	1.957
${}^{13}\text{CO}$		55.101011	0.11046	$\text{C}^{34}\text{S}$		24.103541	1.957
$\text{C}^{17}\text{O}$		56.179990	0.11034	${}^{13}\text{CS}$		23.123856	1.957
$\text{C}^{18}\text{O}$		54.891420	0.11079	HCN	Hydrogen Cyanide	44.315975	2.984
HCO <sup>+</sup>	Oxomethylum	44.5944	3.30	$\text{H}^{13}\text{CN}$		43.170137	2.984
$\text{H}^{13}\text{CO}^+$		43.37722	3.3	$\text{HC}^{15}\text{N}$		43.02769	2.984
$\text{HC}^{18}\text{O}^+$		42.58121	3.30	DCN		36.20746	2.984
DCO <sup>+</sup>		36.01976	3.3	HNC	Hydrogen Isocyanide	45.33199	3.05
HOC <sup>+</sup>	Hydroxymethylidynium	44.7349	4.0	$\text{HN}^{13}\text{C}$		43.54561	2.699
$\text{N}_2\text{H}^+$	Diazenylum	46.586867	3.40	$\text{H}^{15}\text{NC}$		43.02769	2.984
$\text{N}_2\text{D}^+$		38.554719	3.40	DNC		38.152998	3.050
SiO	Silicon Monoxide	21.711967	3.098	$\text{HC}_3\text{N}$	Cyanoacetylene	4.549058	3.724
HCS <sup>+</sup>	Thioxomethylum	10.691406	1.86	$\text{HC}_5\text{N}$	Cyanodiacetylene	1.33133	4.37
HF	Hydrogen Flouride	616.365	1.826	$\text{HC}_7\text{N}$	Cyanohexatriyne	0.5640007	5.0
$\text{C}_3\text{O}$	Tricarbon Monoxide	4.8108809	2.391	$\text{HC}_9\text{N}$	Cyanoctatetrayne	0.2905183	5.6
OCS	Carbonyl Sulfide	6.0814921	0.715	$\text{HC}_{11}\text{N}$	Cyanodecapentayne	0.1690629	6.2

<sup>a</sup>D = Debye. 1D =  $10^{-18}$  esu (cgs units).

References. — All data from JPL line catalog

Astrochemists do not typically present their data like in Figure 4.10. It is hard to analyse and more importantly misses out on molecules that are not-so-abundant. A nicer representation of molecular spectrum is as follows:

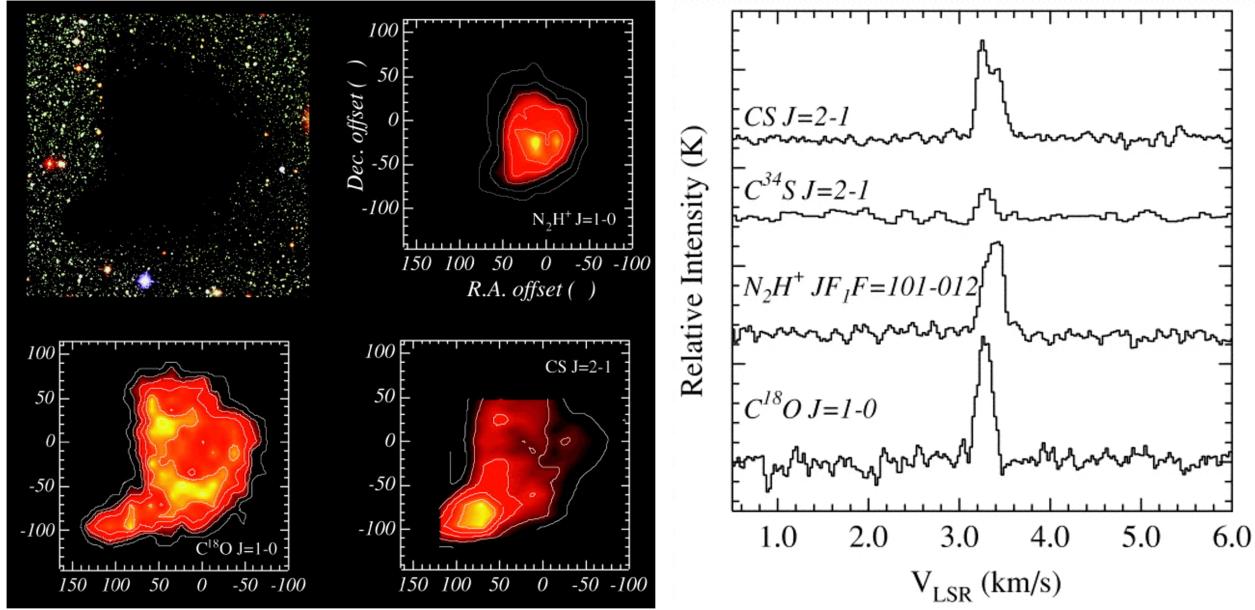


Figure 4.11: Radio images and spectra of B68 taken by the Institut de Radioastronomie Millimetrique (IRAM) 30 m telescope. Image credit: C. J. Lada, 2003, ApJ 568, 286

To obtain the above results, in the authors' words<sup>3</sup>

We used the 30 m IRAM millimeter-wave telescope located at Pico Veleta in Spain for the observations reported here. Observations were obtained during three periods: 2000 April and August and 2001 April. The dual mixer, dual-channel receiver was tuned to observe the  $J = 1/2 - 1/2$  transition of  $\text{C}^{18}\text{O}$  at 109.78218 GHz, the  $1 - 0$  transition of  $\text{N}_2\text{H}^+$  at 93.173178 GHz, and the  $J = 2 - 1$  transitions of  $\text{C}^{32}\text{S}$  at 97.980968 GHz and  $\text{C}^{34}\text{S}$  at 96.412982 GHz. Observations of the  $J = 1 - 0$  transition of  $\text{C}^{17}\text{O}$  and the  $J = 3 - 2$  transition of  $\text{N}_2\text{H}^+$  were also obtained and reported elsewhere.

Although not as widely probed, ro-vibrational spectrums are also taken and analysed by astrochemists. Some examples are shown below.

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<sup>3</sup>C. J. Lada, 2003, ApJ 568, 286

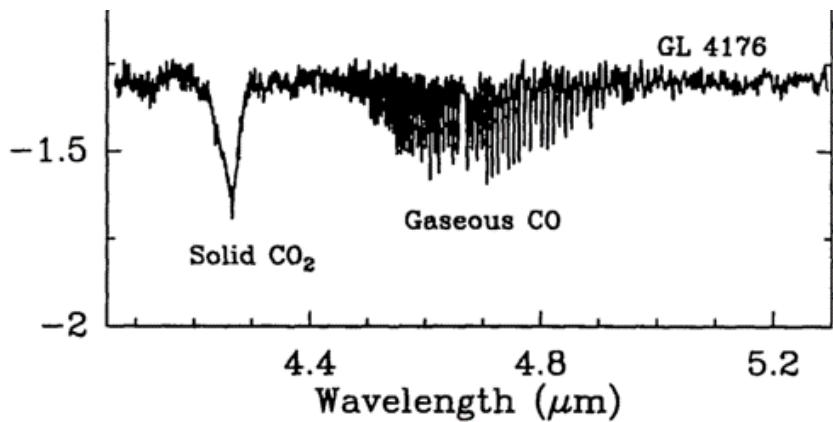


Figure 4.12: IR spectrum of a massive young stellar object AFGL4176 taken by the Infrared Space Observatory (ISO). Note the characteristic P- and R- branches of the rovibrational spectrum of carbon monoxide. The broad peak at  $4.27 \mu\text{m}$  is attributed to solid CO<sub>2</sub>. Image taken from E. F. van Dishoeck et al., 1998, ASP Conf. Ser., 132, 54

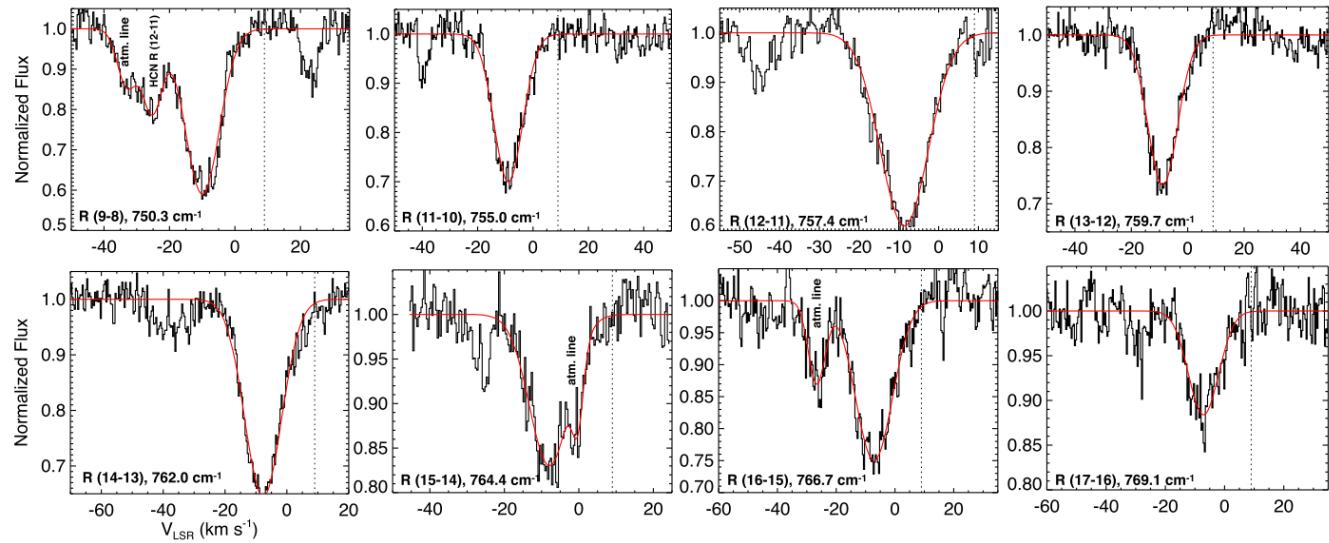
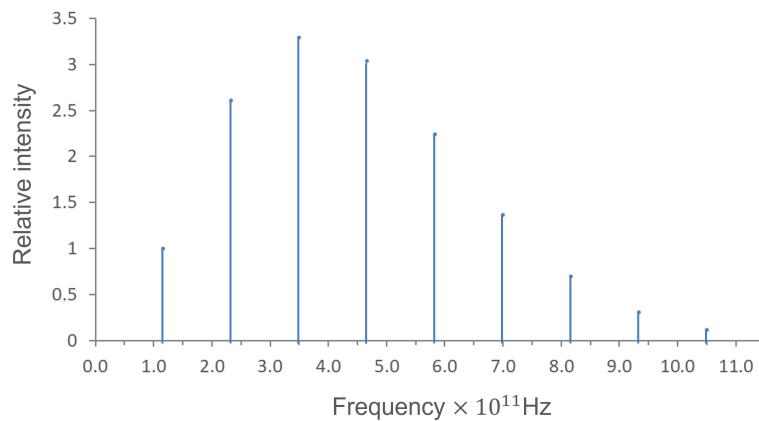


Figure 4.13: Ro-vibrational peaks of Acetylene (C<sub>2</sub>H<sub>2</sub>) taken by EXES onboard SOFIA. Spectra taken from N. Rangwala et al. 2018, ApJ

## 4.5 Discussion Questions

1. Explain how colour can arise from molecules.
2. Electronic transitions for molecules occur in the UV-vis regime.
  - (a) One limitation of UV-vis spectroscopy for molecules is the lack of specificity. Discuss what this means and why this is so.
  - (b) Despite its limitation(s), UV-vis spectroscopy is widely used in research labs. What are some common uses of UV-vis spectroscopy?
3. The figure below is a simulated rotation spectrum of CO. Estimate the internuclei distance of CO.



3. The molecule Cyanoacetylene  $\text{HC}_3\text{N}$  exhibits a spectral line at 9.098 GHz for the  $4 = 1 \rightarrow 0$  transition.
  - (a) What is the rotational constant in units of GHz?
  - (b) In what category of the EM spectrum does this line belong to? (radio/microwave/IR/visible/UV/X-ray)
  - (c) What are the positions of the spectral lines corresponding to the transitions  $J = 2 \rightarrow 1$ ,  $J = 3 \rightarrow 2$ ,  $J = 4 \rightarrow 3$ , etc.?
  - (d) Simulate the rotational (emission) spectrum of Cyanoacetylene  $\text{HC}_3\text{N}$  at  $T = 10$  K, 50 K and 100 K.
5. Derive an expression for the most probable  $J$  transition line for rotational spectroscopy. (Hint: use Eq.(4.27)). Suggest how we can estimate the temperature of the observed object using rotational spectroscopy.
6. By referring to the following figure, suggest why the range of isotopes would result in a different wavenumber.

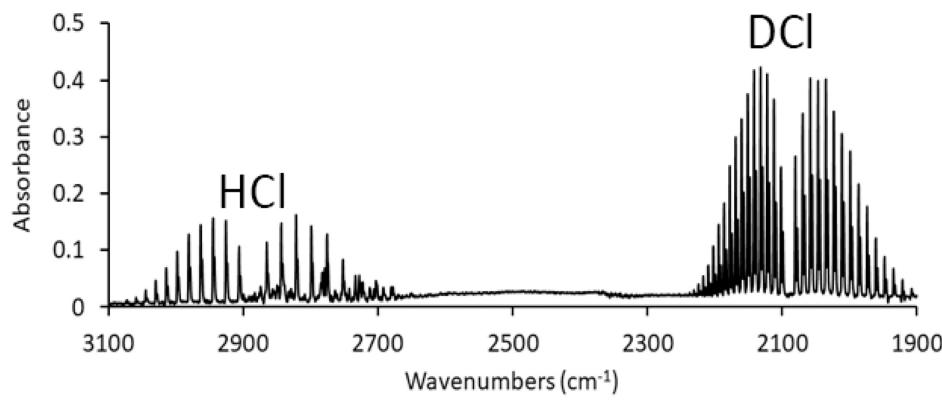
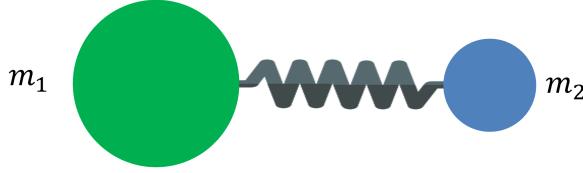


Figure 4.14: Rovibrational Spectrum of HCl and DCl, adapted from J. Chem. Educ. 2018, 95, 12, 2293–2297

## 4.6 Appendix

### 4.6.1 Derivation of 2-mass-1-spring simple harmonic oscillator.



The equations of motion of the two masses are

$$m_1 \ddot{x}_1 = k(x_2 - x_1 - x_0) \quad (4.38)$$

$$m_2 \ddot{x}_2 = -k(x_2 - x_1 - x_0) \quad (4.39)$$

Let  $x_c$  be the center of mass. By principle of moments,

$$m_1(x_c - x_1) = m_2(x_2 - x_c) \quad (4.40)$$

Let  $x_d$  be the distance between the two masses

$$x_d = x_2 - x_1 \quad (4.41)$$

This gives

$$\begin{aligned} m_1 x_c - m_1 x_1 &= m_2(x_d + x_1) - m_2 x_c \\ x_1(m_1 + m_2) &= (m_1 + m_2)x_c - m_2 x_d \\ x_1 &= x_c - \frac{m_2}{m_1 + m_2} x_d \end{aligned} \quad (4.42)$$

Similarly,

$$x_2 = x_c + \frac{m_1}{m_1 + m_2} x_d \quad (4.43)$$

We sought to re-write the equations of motion in terms of  $x_c$  and  $x_d$ . Putting Eq.(4.41), (4.42) and (4.43) into Eq.(4.38) and (4.39), we have

$$\begin{aligned} m_1 \left( \ddot{x}_c - \frac{m_2}{m_1 + m_2} \ddot{x}_d \right) &= k(x_d - x_0) \\ m_2 \left( \ddot{x}_c + \frac{m_1}{m_1 + m_2} \ddot{x}_d \right) &= -k(x_d - x_0) \\ (m_1 + m_2) \ddot{x}_c &= 0 \\ \ddot{x}_c &= 0 \end{aligned}$$

That is a bit of work to show that the center of mass do not accelerate in the vibrational motion! Okay.. but what about the distance of separation? Putting Eq.(4.38) and (4.39) into Eq.(4.41),

$$\begin{aligned} \ddot{x}_d &= \ddot{x}_2 - \ddot{x}_1 \\ &= -\frac{k}{m_2}(x_d - x_0) - \frac{k}{m_1}(x_d - x_0) \\ &= -\frac{m_1 + m_2}{m_1 m_2} k(x_d - x_0) \\ &= -\frac{k}{\mu}(x_d - x_0) \end{aligned}$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the effective mass of the system. The above can be made even simpler by letting  $x = x_d - x_0$  to obtain

$$\ddot{x} = -\frac{k}{\mu}x$$

To obtain the potential energy of the system, we use the force-potential relationship:

$$\begin{aligned} F &= -\frac{dV}{dx} \\ \frac{dV}{dx} &= -\mu \ddot{x} = kx \\ V &= \frac{1}{2}kx^2 \end{aligned}$$

(We can set the constant of integration to zero without loss of generality.)

#### 4.6.2 A note on quantum operators

In the previous chapter, we saw that Schrödinger was inspired by the energy conservation equation

$$\frac{p^2}{2m} + V(x) = E$$

and arrived at the Schrödinger equation

$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E\psi(x)$$

In 3 dimensions,

$$\frac{\mathbf{p}^2}{2m} + V(x) = E$$

where  $\mathbf{p} = (p_x, p_y, p_z)$ , leads to

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where  $\mathbf{r} = (x, y, z)$  and

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

In spherical coordinates,

$$\nabla^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

It turns out to obtain the Schrödinger equation from classical concepts, one can make the following conversions:

$$\begin{aligned} x &\rightarrow x \\ p &\rightarrow -i\hbar \frac{\partial}{\partial x} \\ p^2 &\rightarrow -\hbar^2 \frac{\partial^2}{\partial x^2} \\ \mathbf{r} &\rightarrow \mathbf{r} \\ \mathbf{p}^2 &\rightarrow -\hbar^2 \nabla^2 \end{aligned}$$

The right-hand-side of the above conversions are known as the “operators” in the language of quantum mechanics. For angular momentum  $L$  the operator conversions are

$$\begin{aligned} L_x &\rightarrow -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ L_y &\rightarrow -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ L_z &\rightarrow -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \frac{\partial}{\partial \phi} \\ \mathbf{L}^2 &\rightarrow -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \theta^2} \right] \end{aligned}$$

For the rigid rotor,

$$T + V = \frac{\mathbf{L}^2}{2I} = E$$

gives the SE

$$-\frac{\hbar^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \theta^2} \right] \psi = E\psi$$