

LAB #2: FTIR (ROTATIONAL/VIBRATIONAL) SPECTROSCOPY OF HCl/DCI**Abstract**

High resolution infrared absorption spectra of gaseous HCl and DCI are collected and used to explore the vibrational and rotational energy levels of the two gases.

Related Reading

McQuarrie and Simon, *Physical Chemistry: A Molecular Approach*, Chapter 13, §13-2 to 13-5, "Molecular Spectroscopy," pp. 497-507 and Chapter 5: "The Harmonic Oscillator and the Rigid Rotator: Two Spectroscopic Models," pp. 157-178

Background

The vibrational-rotational spectrum results when rotational transitions accompany vibrational transitions in a molecule. One classical example of this is a spinning ice-skater. As the skater pull her arms closer to her body, she spins faster. Similarly, if you imagine a diatomic molecule, you can see that a decrease in bond length (a vibrational transition) results in faster rotations. Infrared spectroscopy allows you to observe different rotational transitions that occur within a single vibrational transition, and from this data, you can elucidate some important physical information about the molecule.

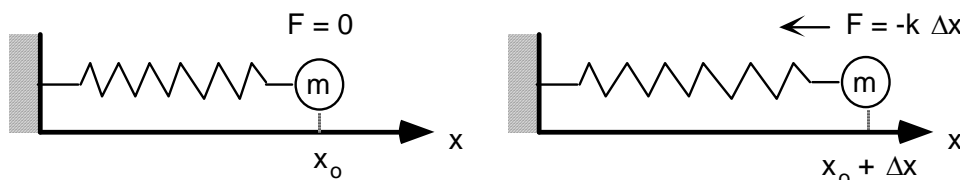
Vibrational-rotational spectroscopy involves two precisely solvable problems: the harmonic oscillator (vibrations) and the rigid rotor (rotations) [see McQuarrie, Chapter 5]. Here, we will review each separately and then see how they are combined to explain the vibrational-rotational spectrum.

Vibrations

If an object can move away from its equilibrium (lowest energy) position against a force proportional to the distance it moves, it is called a harmonic oscillator. A classical harmonic oscillator (such as a mass attached to a spring) can be described by Hooke's Law, which states that the force of a stretched spring is equal to the displacement (Δx) times the force constant (k).

$$F = -k\Delta x \quad (1)$$

Figure 1 shows a spring at rest (1a) and then stretched to some position where a force is now present (1b). If we call the resting position x_0 and the final position x , then displacement, Δx , is equal to $x - x_0$.



1a

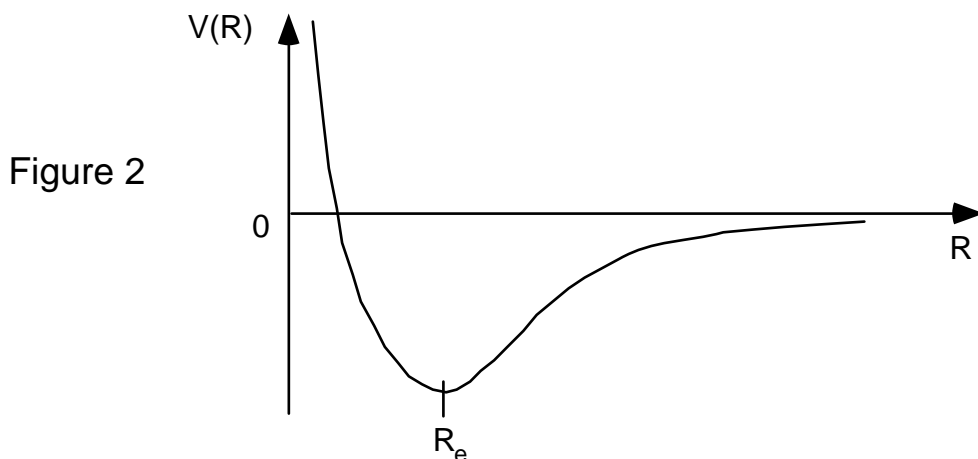
Figure 1

1b

The potential energy of this system is given by minus the integral of equation (1) from x_0 to x . Note the substitution $\Delta x = x - x_0$.

$$V = - \int_{x_0}^x F dx = - \int_{x_0}^x k(x - x_0) dx = \frac{1}{2} k(x - x_0)^2 \quad (2)$$

A chemical bond between two atoms vibrates as a harmonic oscillator. The equilibrium bond length (R_e) is the resting position and any bond length shorter or longer than R_e is like the stretched position of the spring. This is easiest to see in a qualitative potential energy diagram (see Figure 2).



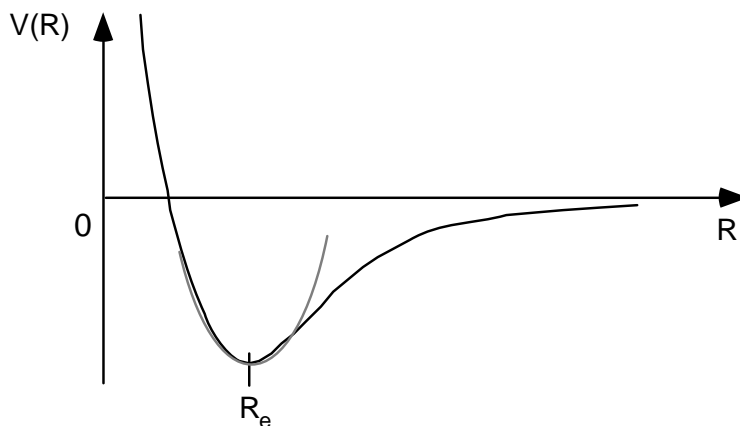
At R_e , the potential energy, $V(R)$, is at its minimum. When R is longer than R_e , the potential energy increases, approaching zero as the bond length goes to infinity. When R is shorter than R_e , the potential energy also increases, approaching infinity as the bond length goes to zero. To find a simple equation to express $V(R)$, we must limit the molecule to a state where the bond length spends most of its time near R_e . In this part of the curve, $V(R)$ can be approximated by a parabolic function:

$$V = \frac{1}{2} k(R - R_e)^2 \quad (3)$$

where $R - R_e$ is the displacement from equilibrium bond length.

Using this mathematical model, we have approximated the potential energy function shown in Figure 2 as a parabola. As you can see in Figure 3, the harmonic oscillator approximation is only valid at values near R_e . As the curve moves away from R_e , the function must be corrected to account for anharmonicity.

Figure 3



The harmonic oscillator approximation can also be evaluated using quantum mechanics. The quantum mechanical solution to the Schrödinger equation for a harmonic oscillator gives a series of quantized energies with the following solutions:

$$E_{\text{vib}} = h\nu_0(v + 1/2) \quad (v = 0, 1, 2, \dots) \quad (4)$$

where v is the vibrational quantum number and

$$\nu_0 = 1/2\pi (k/m)^{1/2} \quad (5)$$

ν_0 is called the vibrational frequency. k is the force constant and m is the mass of the atom. Different values of v designate different “vibrational states” of the system, and give rise to different energies, all of which are multiples of ν_0 . In the case of a heteronuclear diatomic molecule, equation (5) must be adjusted to accommodate two different masses. The reduced mass, μ , is substituted for m .

$$\mu = m_A m_B / (m_A + m_B) \quad (6)$$

where m_A is the mass of one atom and m_B is the mass of the other. The vibrational frequency is then defined:

$$\nu_0 = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \text{ s}^{-1} \quad (7)$$

In wavenumbers, the energy, $G(v)$, and the vibrational frequency, $\tilde{\nu}_0$, are:

$$G(v) = \tilde{\nu}_0 \left(v + \frac{1}{2} \right) \text{ cm}^{-1} \quad \text{and} \quad \tilde{\nu}_0 = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \text{ cm}^{-1} \quad (8)$$

Transitions among vibrational levels are subject to the selection rule that $\Delta v = \pm 1$ and the dipole moment of the molecule must vary during a vibration.

Rotations

While the harmonic oscillator model considers a bond like two masses connected by a flexible spring, the rigid rotor model considers a bond like two masses connected by a rigid bar, like a dumbbell. The dumbbell rotates as a unit, and the energies of rotation are also solvable by quantum mechanics [see McQuarrie, Chapter 5]:

$$E_{\text{rot}} = B_e J(J + 1) \quad (J = 0, 1, 2, \dots) \quad (9)$$

Here, J is the rotational quantum number and B_e is the rotational constant and is defined:

$$B_e = \left(\frac{h}{8\pi^2 \mu R_e^2} \right) = \left(\frac{h}{8\pi^2 I} \right) \text{ s}^{-1} \quad (10)$$

where μ is the reduced mass (as defined in equation (6)) and R_e is the equilibrium bond length for a vibrating diatomic molecule (if the rotor were truly rigid, the bond length would be constant).

In wavenumbers, the energy, $F(J)$, and the rotational constant, \tilde{B} , are:

$$F(J) = \tilde{B}J(J+1) \text{ cm}^{-1} \quad \text{and} \quad \tilde{B}_e = \frac{h}{8\pi^2 cI} \text{ cm}^{-1} \quad (11)$$

Rotational transitions are governed by the selection rule $\Delta J = \pm 1$ and the molecule must have a permanent dipole moment.

Vibrations and Rotations

When we consider both rotations and vibrations simultaneously, we take advantage of the fact that these transitions occur on different timescales. Typically, a molecular vibration takes on the order of 10^{-14} s. A molecular rotation is normally much slower, taking on the order of 10^{-9} or 10^{-10} s. Hence, as a molecule rotates one revolution, it vibrates many, many times. Since the vibrational energies are large compared with the rotational energies, the appropriate energy level diagram is:

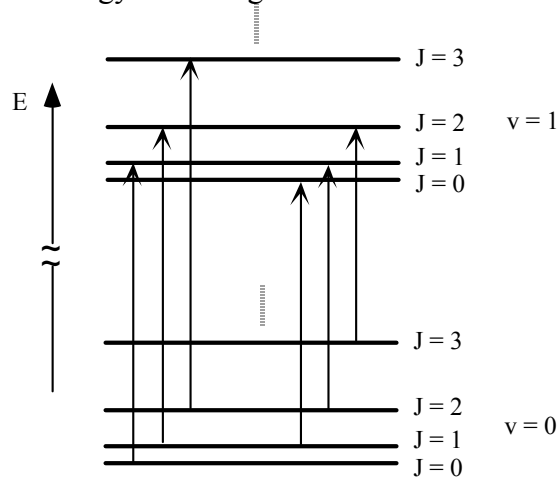


Figure 4

The spectroscopic transitions you will observe in this experiment correspond to arrows pictured in the diagram. The spacing between vibrational (v) energy levels is large compared to the spacing between rotational (J) energy levels. As a result, all the peaks you observe will be of the vibrational transition $\Delta v = +1$. You will need to assign the rotational transitions based on the selection rule, $\Delta J = \pm 1$. This simplifies your spectral assignment, since it rules out any transitions which don't follow the rule (such as $J = +2$).

There is an interaction between the rotations and vibrations, causing \tilde{B} to be dependent on v . Thus, the total energy in the rigid-rotator harmonic-oscillator model is:

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}_0(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \quad (12)$$

where $v = 0, 1, 2 \dots$ and $J = 0, 1, 2 \dots$. \tilde{B}_0 is the rotational constant when $v = 0$ and \tilde{B}_1 is the rotational constant when $v = 1$. It is often useful to relate \tilde{B}_v to \tilde{B} , allowing a direct calculation of R_e :

$$\tilde{B}_v = \tilde{B} - \tilde{\alpha}_e(v + \frac{1}{2}) \quad v = 0, 1, 2, \dots \quad (13)$$

The energy of observed transitions, $\tilde{\nu}_{obs}$, can be calculated from Eq (12):

$$\tilde{\nu}_{obs}(\Delta J = +1) = \tilde{E}_{v+1,J+1} - \tilde{E}_{v,J} = \tilde{\nu}_0 + \tilde{B}_1(J+1)(J+2) - \tilde{B}_0 J(J+1) \quad (14)$$

$$\tilde{\nu}_{obs}(\Delta J = -1) = \tilde{E}_{v+1,J-1} - \tilde{E}_{v,J} = \tilde{\nu}_0 - \tilde{B}_1 J(J-1) - \tilde{B}_0 J(J+1) \quad (15)$$

Substituting Eq (13) into Eqs (14) and (15), the final expressions for the two types of transitions are determined:

$$\tilde{\nu}_{obs}(\Delta J = +1) = \tilde{\nu}_0 + 2\tilde{B}(J+1) - (J+1)(J+3)\tilde{\alpha}_e \quad (16)$$

$$\tilde{\nu}_{obs}(\Delta J = -1) = \tilde{\nu}_0 - 2\tilde{B}J - J(J-2)\tilde{\alpha}_e \quad (17)$$

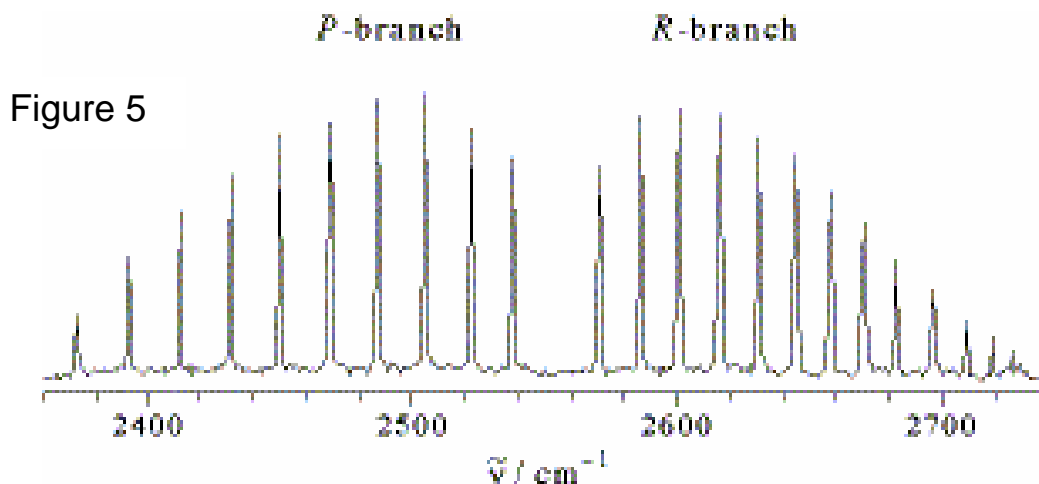
Equations (16) and (17) can be simplified by substituting $n = J+1$ in equation (16) and $n = -J$ in equation (17), the result is an identical equation:

$$\tilde{\nu}_{obs} = \tilde{\nu}_0 + 2(\tilde{B} - \tilde{\alpha}_e)n - \tilde{\alpha}_e n^2 \quad (18)$$

Equation (18) allows one to plot the results for both branches on one graph. Fitting the data to a quadratic formula will allow one to determine values for \tilde{B} and $\tilde{\alpha}_e$. From these values, $\tilde{\nu}_0$, R_e , and k can be determined from equations found above.

Example Spectra (and more info)

Figure 5 shows the vibrational-rotational infrared spectrum of HCl. By convention, a series of transitions for which $\Delta J = -1$ is called a **P branch**, and a series of lines for which $\Delta J = +1$ is called an **R Branch**. An R branch transition originating in state J and terminating in state $J+1$ is written "R(J)", and a P branch transition originating in state J and terminating in state $J-1$ is written "P(J)". (Q branches, in which $\Delta J = 0$ can occur in some cases, but not in the vibrational-rotational spectra of diatomic molecules, so we will ignore them.) The gap between the R branch and P branch corresponds to $\tilde{\nu}_0$, and the separation of the lines in both branches is $\sim 2\tilde{B}$. Example 13-3 from McQuarrie gives an example of using this information to predict the spectra of diatomic gases.



If one examines Figure 5 closely, it becomes apparent that the lines of the R-branch are more closely spaced than the P-branch lines. In addition, if one would compare the experimental values obtained for $\tilde{\nu}_0$ and \tilde{B} with those calculated by the above equations, some fairly severe discrepancies would be apparent, especially at increasing values of J and v . The discrepancies basically arise from three factors: the increase in vibrational amplitude with increasing vibrational states (this is why \tilde{B} depends on v), the reality that chemical bonds are not truly rigid (i.e., the bonds stretch slightly upon rotation), and the anharmonicity of the internuclear potential energy well. Mathematically, there are several additions made to Eqs (13) and (14) to account for these discrepancies. §13-3, 13-4 and 13-5 of McQuarrie explain these mathematical terms and show how they are obtained.

With these additional terms, the total energy becomes

$$\tilde{E}_{tot} = \tilde{\nu}_e \left(v + \frac{1}{2} \right) + \tilde{B}_v J(J+1) - \tilde{D} J^2 (J+1)^2 - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 \quad (19)$$

where v and J are quantum numbers equal to 0, 1, 2, ..., and is the frequency of the molecule vibrating around the equilibrium internuclear separation, R_e . \tilde{D} is the centrifugal distortion constant and \tilde{x}_e is an anharmonicity constant. Refer to McQuarrie for more detailed information. When including the centrifugal distortion constant, \tilde{D} , Eq (18) becomes:

$$\tilde{\nu}_{obs} = \tilde{\nu}_0 + 2(\tilde{B} - \alpha_e)n - \tilde{\alpha}_e n^2 - 4\tilde{D}n^3 \quad (20)$$

Procedure

Safety and Other Concerns: Follow general lab safety rules. The KBr windows of the IR cell are hygroscopic. Do not touch them and keep the cell in the desiccator when not in use.

In the Lab: HCl (and DCl) gas is placed in a cell with KBr windows. The KBr windows are used because glass absorbs strongly in the infrared region. We will use the Nicolet FT-IR to record the IR spectrum of HCl (and DCl). More details will be available in lab.

Analysis:

All aspects of the data analysis are described in the Background section. Make sure you understand how the equations are derived and what the constants $\tilde{\alpha}_e$, \tilde{B} , ν_0 , R_e , and k represent. (You will need to justify your calculations in your lab report).

- Assign each peak to a specific rotational transition (R(0), P(1), ...)
- Using the index, n (P branch: $n = -J$; R branch $n = J + 1$), tabulate the values of n and the corresponding $\tilde{\nu}$ (in wavenumbers) of the transition.
- Plot $\nu_{obs}(n)$ against n using Eq. (18). Look for outliers.
- Use Sigmaplot or other program and Eq (18) above to get ν_0 , $(2\tilde{B} - 2\tilde{\alpha}_e)$, \tilde{B} , and $\tilde{\alpha}_e$ for all isotopic species. Repeat with Eq (20) to get ν_0 , $(2\tilde{D} - 2\tilde{\alpha}_e)$, \tilde{B} , $\tilde{\alpha}_e$, and \tilde{D} . Compare the values obtained from each fit.
- Use \tilde{B} and $\tilde{\alpha}_e$, and any combination of equations above, to find R_e and k for HCl. Compare R_e and your other constants to the latest data at NIST Webbase (<http://webbook.nist.gov/chemistry/>).
- Calculate the moment of inertia for HCl.
- Using the two isotopic peaks (H^{37}Cl and H^{35}Cl or H^{35}Cl and D^{35}Cl) compute the ratio of \tilde{B} for the two isotopes. Use Table 1 for correct isotopic masses. Which isotopic substitution (^{37}Cl for ^{35}Cl or D for H) affects \tilde{B} more?
- Determine the temperature of the sample using the Boltzmann equation and the peak in the rotational contour (what is the most populated rotational state, J_{mp} , and how does this relate to the temperature). [Hint: See McQuarrie §18-5]
- Simulate a spectrum using 1 cm^{-1} resolution and Gaussian functions to simulate the individual lines. Do this at two temperatures 600 K and 300 K. Use mathcad file [gaussian_spectrum.mcd](#) as a template for this calculation. (www.gustavus.edu/academics/chem/pchem/gaussian_spectrum.mcd)

Table 1

	atomic mass (in amu)	isotopic abundance (%)
^1H	1.007825	99.985
^2H	2.0140	0.015
^{35}Cl	35.968852	75.77
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

References

1. McQuarrie, D. A.; Simon, J. D.; *Physical Chemistry: A Molecular Approach*, University Science Books: Sausalito, CA, 1997.
2. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*; 6 ed. McGraw-Hill: New York, 1996.
3. Gentry, W. R., Buttrill, S. E., Crawford, B., et al. *Chemistry 4511 Advanced Physical Chemistry Lab Manual*, 18th ed., August 2006.