Vibrational-Rotational Spectra of HCl Gas

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Abstract: In this lab the FTIR spectrum was taken of purified HCl gas through an analysis of its spectrum its properties were able to be determined. The sample was analyzed and had a fundamental wave number of 2885 cm⁻¹, an alpha (α) constant of 0.301, a Bₚ constant of 10.511, and a Dₑ constant of 2.2 x 10⁻⁹. From this information the moment of inertia was determined to be 2.659 x 10²¹, the bond length of the molecule was 5.229 x 10⁻¹⁰ cm, the fundamental vibrational frequency was 2984 cm⁻¹, and the anharmonicity constant was determined to have a value of 50.

bond length = 1.21 Å
Introduction:

In this laboratory the infrared vibrational spectrum of the linear molecule hydrochloric acid was taken and analyzed to obtain the moment on inertia for the molecule and consequently the intermolecular separation. Also the force constant, which is a measure of the hydrogen chloride bond strength, was also obtained.

When considering a vibrating diatomic molecule one can say that the simplest form of such a system is that of the harmonic oscillator. In this sort of system the potential energy depends only quadratically on the change in internuclear distance and nothing else. This produces the known energy levels for the harmonic oscillator from quantum mechanics and they follow the form:

\[ E(v) = \hbar v(v + \frac{1}{2}) \]

Where \( v \) is equal to the vibrational quantum number

\( v \) is the vibrational frequency

and \( \hbar \) is equal to Planck’s constant

When considering the simplest form of a rotating diatomic system, the dumb-bell system can be considered. In this type of system the two masses of the system, \( m_1 \) and \( m_2 \) are said to be joined by a rigid weightless rod, which in our case represents a bond. Through the use of quantum mechanics it can be seen that the allowed energy levels for this system are as follows:

\[ E(J) = \left(\frac{\hbar^2}{8\pi^2 I}\right)J(J+1) \]

Where \( J \) is the rotational quantum number

\( I \) is the moment of inertia

Since the moment of inertia is related to the internuclear distance, \( r \), and the reduced mass, \( \mu \), the following can be obtained.

\[ \mu = m_1m_2/(m_1 + m_2) \]

and then \( I = \mu r^2 \)

Now this gives the simplest form of both the vibrational and rotational systems independently, but since real molecules undergo both of these at the same time we must formulate and expression to deal with this scenario. A sum of the two energies would produce the following expression:

\[ E_{v,J} = \hbar v(v + \frac{1}{2}) + [J(J+1)/2I]\hbar^2 \]
However, this is not a good approximation and therefore the following equation is produced for the energy levels of the system:

\[ T_{\nu,J} = E_{\nu,J}/hc = \vec{v}_{e}(\nu + \frac{1}{2}) - \vec{v}_{e}x_{e}(\nu + \frac{1}{2})^2 + B_{e}J(J + 1) - D_{e}J^2(J + 1)^2 - \alpha_{e}(\nu + \frac{1}{2})J(J + 1) \]

Where the energy levels are expressed in term values \( T \) in units cm\(^{-1} \), \( c \) is the speed of light in cm/s, \( \vec{v}_{e} \) is the wave number in units cm\(^{-1} \), and \( B_{e} = h/8\pi^2I_{p}c \).

In this term the term with the \( x_{e} \) value takes into account the effect of anharmonicity, while the term involving the constant \( D_{e} \) is a correction factor for centrifugal stretching but in the further calculations this term will be omitted. Finally the last portion of the term above accounts for the interaction between vibration and rotation and although the constant \( \alpha_{e} \) is quite small it can not truly be neglected in this case.

Now that the proper energy level equation has been produced one must consider the specific selection rules for both the change in frequency and the change in \( J \). In general the section rules state that \( \Delta\nu = \pm 1 \) and \( \Delta J = \pm 1 \) which basically states that infrared absorption or emission can only occur when these “allowed” transitions take place. In the case of this lab we are interested in the most intense absorption band which means we are concerned with transitions from various \( J'' \) levels of the vibrational ground state, \( \nu'' = 0 \), to \( J' \) levels in the first excited vibrational state, \( \nu' = 1 \).

When we combine the selection rules with this information we know that the transition must be from \( J'' \) to \( J' \) and equal to \( J'' = J' \pm 1 \) and since \( \Delta E = h\nu = hc\vec{v} \) the frequency for this transition will be \( T(\nu',J') - T(\nu'',J'') \). When \( \Delta J = +1 \) \( (J' = J'' + 1) \) and correspondingly when \( \Delta J = -1 \) \( (J' = J'' - 1) \) we can find the equations for the lines of the R and P branches of the spectra.

Starting with the fact that:

\[ \vec{v}_R = T(\nu',J') - T(\nu'',J'') \]

\[ T_{\nu,J} = \vec{v}_{e}(\nu + \frac{1}{2}) - \vec{v}_{e}x_{e}(\nu + \frac{1}{2})^2 + B_{e}J(J + 1) - D_{e}J^2(J + 1)^2 - \alpha_{e}(\nu + \frac{1}{2})J(J + 1) \]

We substitute and omit the \( D_{e} \) term from the equation to produce the following:

\[ \vec{v}_R = [\vec{v}_{e}(\nu + \frac{1}{2}) - \vec{v}_{e}x_{e}(\nu + \frac{1}{2})^2 + B_{e}J(J' + 1)(J'' + 2) - \alpha_{e}(\nu' + \frac{1}{2})J'(J' + 1)] - [\vec{v}_{e}(\nu'' + \frac{1}{2}) - \vec{v}_{e}x_{e}(\nu'' + \frac{1}{2})^2 + B_{e}J''(J'' + 1)(J' + 2) - \alpha_{e}(\nu'' + \frac{1}{2})J''(J'' + 1)] \]

And knowing that for the transition we are investigating \( \nu' = 1 \) and \( \nu'' = 0 \) we can produce the following equations:
\[ T(1, J') = \varphi_d(3/2) - \varphi_e x_e (3/2)^2 + B_e J'(J' + 1) - \alpha_e (3/2) J'(J' + 1) \]
\[ T(0, J') = \varphi_d(1/2) - \varphi_e x_e (1/2)^2 + B_e J''(J'' + 1) - \alpha_e (1/2) J''(J'' + 1) \]

And because \( J' = J'' + 1 \)

The \( T(1, J') \) equation can be rewritten:
\[ T(1, J') = \varphi_d(3/2) - \varphi_e x_e (3/2)^2 + B_e (J'' + 1)(J'' + 2) - \alpha_e (3/2)(J'' + 1)(J'' + 2) \]

And we combine the two equations using the form \( \varphi_R = T(v', J') - T(v'', J'') \) to get:
\[ \varphi_R = [\varphi_d(3/2) - \varphi_d(1/2)] - [\varphi_e x_e (3/2)^2 - \varphi_e x_e (1/2)^2] + B_e [J''^2 + 3 J'' + 2 - J''^2 - J''] - \alpha_e [3/2(J''^2 + 3J'' + 2) - \frac{1}{2}(J''^2 + J'')] \]
\[ \varphi_R = \varphi_e - \varphi_e x_e [3-1] + 2B_e (J'' + 1) - \alpha_e [3/2 J''^2 + 9/2 J'' + 3 - 1/2 J'' - \frac{1}{2} J''] \]
\[ \varphi_R = \varphi_e - 2 \varphi_e x_e + 2B_e (J'' + 1) - \alpha_e [J''^2 + 4J'' + 3] \]
\[ \varphi_R = \varphi_e - 2 \varphi_e x_e + 2B_e J'' + 2B_e - \alpha_e J''^2 - 4\alpha_e J'' - 3\alpha_e \]
\[ \varphi_R = \varphi_e - 2 \varphi_e x_e + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e) J'' - \alpha_e J''^2 \]

And if we let \( \varphi_e - 2 \varphi_e x_e = \varphi_0 \) we get the final R branch equation:
\[ \varphi_R = \varphi_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e) J'' - \alpha_e J''^2 \]

Now to get the P branch equation we use the same relations we started with above except we will use \( J' = J'' - 1 \) instead of \( J' = J'' + 1 \). Therefore the new \( T(1, J') \) would be equal to:
\[ T(1, J') = \varphi_d(3/2) - \varphi_e x_e (3/2)^2 + B_e (J''-1) J'' - \alpha_e (3/2)(J''-1) J'' \]

And \( T(0, J'') \) stays the same @:
\[ T(0, J'') = \varphi_d(1/2) - \varphi_e x_e (1/2)^2 + B_e J''(J'' + 1) - \alpha_e (1/2) J''(J'' + 1) \]

And because \( \varphi_p = T(v', J') - T(v'', J'') \)
\[ \varphi_p = [\varphi_d(3/2) - \varphi_d(1/2)] - [\varphi_e x_e 3 - \varphi_e x_e 1] + B_e [J''^2 - J'' - J''^2 - J''] - \alpha [3/2 J''^2 + 3/2 J'' - 1/2 J''^2 - 1/2 J''] \]
\[ \varphi_p = \varphi_e - 2 \varphi_e x_e + B_e (-2J'') - \alpha_e [J''^2 - 2J''] \]
\[ \varphi_p = \varphi_e - 2B_e J'' - \alpha_e J''^2 + \alpha_e 2J'' \]
\[ \varphi_p = \varphi_0 - \alpha_e J''^2 - J''(2B_e - \alpha_e) \]
Now we can take the two equations for the R and P branch and combine them into one equation if we introduce a new quantity, m. Where \( m = J'' + 1 \) for the R branch and \( m = -J'' \) for the P branch. The new single equation would have the form:

\[
\tilde{D}_{(m)} = \tilde{D}_0 + (2B_0 - 2\alpha_e) m - \alpha_e m^2
\]

Where \( m \) takes all integral values and \( m = 0 \) yields the forbidden, purely vibrational, transition. From this equation we are able to perform a linear regression in order to obtain the values for \( \tilde{D}_0 \), \( B_0 \), \( \alpha_e \), \( D_e \), \( \tilde{D}_0 \times e \) and \( \tilde{D}_e \).

**Experimental:**

The FTIR spectrum was taken of hydrochloric gas and the spectrum was then printed out for analysis. The guidelines for the calculations and analysis can be found in the laboratory handout “Vibrational-Rotational Spectra of HCl and DCl.” The instructions on how to operate the FTIR can be found in the additional handouts “FTIR Notes” which was handout to the class at the beginning of the lecture.

Multiple FTIR runs were to have been done, but with the presence of a fire drill during the laboratory period, there simply wasn't enough time to run more then the single spectra.

**Results and Discussion:**

In this laboratory the major piece of work that needed to be done, was the production of the FTIR spectrum for the hydrochloric gas sample. This was done by first evacuating a vessel in which the gas could be placed into and taking the baseline spectrum for this evacuated container. Once the baseline spectrum was taken, the gas could be added to the vessel and the FTIR spectrum was able to be taken. The spectrum that was produced for the hydrochloric gas sample can be seen as the attached figure 1.

Once the spectrum was produced the next thing to do was to analyze the spectrum to determine the initial wave number, \( \tilde{D}_0 \), and the constants \( B_0 \) and \( \alpha_e \). To do this the first thing that needed to be done was the assigning of the m values to the spectrum. These m values can be seen at the bottom of the produced spectrum, figure 1. It is important to notice that unlike the spectrum seen in the laboratory handout the R branch of our spectrum is on the left hand side and the P branch is on the right hand side. This is simply a product of the "x" scale being used on the spectral print out. Our wave numbers increase as you move left, and therefore the R branch is on the left hand side.

Once the m values were all determined a table was produced, table 1, listing the m values and their corresponding wave numbers to the nearest tenth of a reciprocal centimeter. From this
table a graph was produced of the wave number vs. their corresponding m values, which can be seen as figure 2. The data on the graph was analyzed and two different equations for two different trend lines were determined. When the trend line was first analyzed as a polynomial to the second power, the equation of the line was determined to be, \( y = -0.301x^2 + 20.37x + 2884 \). Then when the trend line was produced for a polynomial to the third power the equation that was produced was \( y = -0.001x^3 - 0.301x^2 + 20.55x + 2884 \).

When using the first line, and therefore the first equation we were able to determine the \( \bar{v}_0, B_e, \) and \( \alpha_e \) for the gas. This can be done because we know the general equation for the wave number as it depends on m is as follows:

\[
\bar{v}(m) = \bar{v}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2
\]

This means that our equation directly fits into this form and tells us that our fundamental wavenumber is equal to 2884 cm\(^{-1}\) and if we look at the produced spectra this number is right between m = -1 and m = 1 which means that this number can be taken as true, and we can from here also assume that the other results are good results because they come from this equation.

Next we know that the \( \alpha_e \) value is 0.301 and therefore from here we can determine the \( B_e \) value. Which through simple algebra turns out to be equal to 10.486. These two numbers are simply constants in the large energy equation and really don’t yield us with any further very important information.

Now if we look at the other equation we have, which this time is to the third power we can determine the \( D_e \) constant. In this case the term to the third power is equal to the \( D_e \) constant while, everything else represents the same thing it did before. Therefore, we get a \( D_e \) value of 2.5 \( \times \) 10\(^{-4} \) which tells us exactly why we omitted it from our earlier derivation. The number is so small that it really has no impact on the equation as a whole and that is why it is left out in previous calculations. And as we see from the rest of the equation the only number it’s presence changes is the \( B_e \) constant and it would only change this value from 10.486 to 10.576. Since the wavenumber and the alpha constant stay the same it can be said that the \( D_e \) constant is needed for perfect accuracy, but for basic assumptions and calculations it can be omitted from derivations and has a negligible effect as a whole on the equation.

From the information we have now obtained we can get the moment of Inertia \( I \), by plugging in the information in to the equation for \( B_e \):$$B_e = \frac{h}{8\pi^2 I_e}$$

\[I = 2.659 \times 10^{27} \text{ (if we use and avg. value for } B_e \text{ from the two values we obtained)}\]
From the moment of inertia we can further determine the internuclear distance $r$, by plugging the needed information into the equation:

$$I = ur^2$$ where $m_1 = 1$ and $m_2 = 35.45$

$$r = 5.229 \times 10^{-10} \text{ cm}$$

$$r = 1.31 \AA$$

In this case is equal to the bond distance between the two atoms in our system, hydrogen and chloride. Now the only thing left to be calculated is the fundamental vibrational frequency and the anharmonicity constant. To do this we must utilize the two equations in which we know about overtones:

$$2884 = \nu_e[1 - x_e2]$$

Which becomes $2884 = \nu_e - 2\nu_e x_e$

And the other equation: $5668 = 2\nu_e [1 - x_e3]$

Which becomes: $5668 = 2\nu_e - 6\nu_e x_e$

We can then use the two equations together to obtain the values we need. To do this the first equation will be multiplied by -2 and then added to the second equation as follows:

$$-5768 = -2\nu_e + 4\nu_e x_e$$

$$5668 = 2\nu_e - 6\nu_e x_e$$

$$-100 = -2\nu_e x_e$$

$$\nu_e x_e = 50$$

We can then plug back in and obtain the $\nu_e$ value.

$$2884\nu_e - 2(50)$$

$$\nu_e = 2984$$

All of the information we have obtained from the spectrum is useful in identifying different qualities and characteristics of the molecule in which we are studying. In this case we have performed the analysis on HCl gas, but many other molecules can be used as long as they are in the gaseous form. The information can also be sued to compare different samples of the
same gas to determine if its properties have changed or to see if the gas has been contaminated in any way.

The FTIR technique is a useful tool in studying different gaseous molecules and their properties with relative ease. Although the calculations associated with the spectrum can be tedious at points they yield a wealth of information and are a useful tool in lab sample analysis.

References:


2. “Vibrational – Rotational Spectra of HCl and DCI” handout
## FTIR Spectrum Analysis

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Wave number vs m

\[ y = 0.001x^3 - 0.301x^2 + 2.05x + 2.884. \]