

Vibrational and Rotational Spectroscopy of Diatomic Molecules

Spectroscopy is an important tool in the study of atoms and molecules, giving us an understanding of their quantized energy levels. These energy levels can only be solved for analytically in the case of the hydrogen atom; for more complex molecules we must use approximation methods to derive a model for the energy levels of the system. In this paper we will examine the vibration-rotation spectrum of a diatomic molecule, which can be approximated by modeling vibrations as a harmonic oscillator and rotations as a rigid rotor. We will use these models to understand the features of the vibration-rotation spectrum of HCl, allowing us to use the spectrum to learn about properties of the molecule.

Keywords: Spectroscopy; Diatomic Molecules; Rotation; Vibration; Quantum Mechanics.

I. INTRODUCTION

Spectroscopy is the study of how matter interacts with electromagnetic radiation. Atoms and molecules interacting with light will sometimes emit photons at specific frequencies; these frequencies depend on the energy level separation for whatever transitions caused the photon emission. We can use this to learn about the energy levels of an atom or molecule.

However, the wavefunctions describing the energy levels of atoms and molecules more complex than hydrogen cannot be solved analytically. A good starting point for analyzing and predicting energy levels is to consider the energy transitions between vibrational and rotational states in diatomic molecules. These transitions are small enough that the molecular orbitals of electrons don't change [1].

Figure 1 shows the experimentally-obtained spectrum of transitions between the ground and first excited vibrational states of HCl [4]. Contained in that spectrum is valuable information allowing us to find the bond length and stiffness of HCl [1]. In order to extract this information, however, we must first understand where the features of the spectrum come from. Our goal will be to understand the physics behind Figure 1; with that knowledge, we will be able to calculate the bond length and stiffness of HCl from this spectrum.

II. SPECTROSCOPY BACKGROUND

A typical spectroscopy experiment will involve a source of photons being directed through a chamber filled with our molecule of interest in gaseous form. For pure rotational spectroscopy, where the only transitions observed are transitions between different rotational states, the photons are typically in the microwave region of the electromagnetic spectrum. Infrared light is typical for vibration-rotation transitions, which involve changing both the vibrational and rotational energy states [1].

In the experiment described above, the energy of photons that is emitted via stimulated emission from the molecule are measured. Our HCl spectrum in Figure 1 is a plot of photon frequency vs. number of photons; a peak at a particular frequency ν indicates that lots of photons were emitted with frequency ν , suggesting that there is

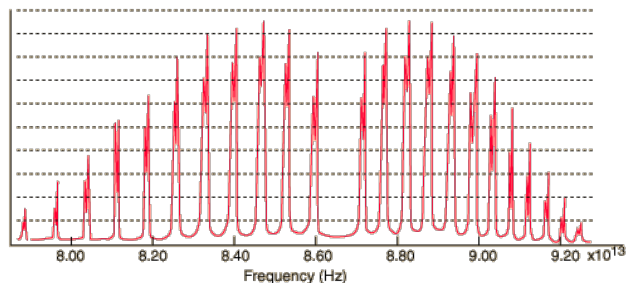


FIG. 1: This is the vibration-rotation spectrum of HCl. The goal of this paper is to explain the physics behind the spectrum. This image was taken from [4].

an energy transition with a change in energy equal to $h\nu$, where h is Planck's constant.

Since we are examining the transitions between energy eigenstates, we will need to determine what energy transitions in our system are allowed. To determine the allowed transitions, we will calculate the Einstein coefficient for stimulated emission, B_{ab} [2]. Consider a molecule with states $|a\rangle$ and $|b\rangle$ with energies E_a and E_b , $E_a < E_b$. A photon with energy equal to $E_b - E_a$ will, half of the time, cause the molecule to transition from state $|b\rangle$ down to state $|a\rangle$, emitting another photon with energy $E_b - E_a$. We can detect this second photon and measure its frequency.

The coefficient B_{ab} is proportional to the probability that a particular transition will occur. Einstein found that

$$B_{ab} = \frac{4\pi^2}{3\hbar^2} |\langle a | \mathbf{d} | b \rangle|^2 \quad (1)$$

where \mathbf{d} is the dipole moment [2]. We see that if $\langle a | \mathbf{d} | b \rangle$ is zero, then that transition will never occur. Thus we can determine the allowed energy transitions by identifying the set of transitions with non-zero transition dipole moments.

III. SIMPLE MODELS OF VIBRATIONS AND ROTATIONS

The vibrations and rotations of a diatomic molecule can be quite simply modeled using the harmonic oscillator

and the rigid rotor, respectively, two exactly-solvable quantum systems. With this alone, a relatively accurate understanding of the HCl spectrum can be reached.

A. Vibrations Modeled as the Harmonic Oscillator

The potential felt by atoms in a diatomic molecule like HCl is not a perfect harmonic potential. Assuming the true potential is $V(r)$ for some internuclear distance r , we can perform a Taylor expansion of $V(r)$ about r_e , the equilibrium distance:

$$V(r) = V(r_e) + V'(r_e)(r - r_e) + V''(r_e)(r - r_e)^2 + \dots \quad (2)$$

For small vibrations about equilibrium, we approximate $V'(r_e) = 0$. We can also define $V(r_e) = 0$ since we only care about relative energies. For small vibrations ($r - r_e \ll 1$), we can ignore terms with higher than second order in r . Thus, we arrive at $V(r) \approx V''(0)r^2 \equiv \frac{1}{2}kr^2$.

From this we can imagine a simplified model of a diatomic molecule in which the two atoms are point masses with mass m_1 and m_2 connected by a spring with spring constant k . From classical mechanics, we find the differential equation describing their motion to be

$$\frac{d^2x}{dt^2} = -\left(\frac{k}{\mu}\right)x \quad (3)$$

where x is the distance between the two spheres and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (4)$$

is the reduced mass of the system [1].

This suggests that, if we model the molecule vibrations as a harmonic oscillator, we should arrive at the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}\mu\omega_e^2\hat{x}^2, \quad \omega_e = \left(\frac{k}{\mu}\right)^{1/2} \quad (5)$$

Our energy eigenstates will therefore have energy

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right), \quad v = 0, 1, 2, \dots \quad (6)$$

where we define v as the quantum vibrational number. Note that ω_e is dependent on the masses of the atoms, not simply the masses of their bare nuclei; in these vibrational models, the electrons are considered close to the nuclei such that they vibrate along with the entire atom [3].

We see that the vibrational energy levels are equally spaced, each one $\hbar\omega_e$ above the previous level. In order to determine the energy of photons emitted during energy transitions, we must first determine the allowed transitions. From equation (1), we know that a non-zero change in dipole moment corresponds to an allowed transition. We write

$$\mathbf{d}_{vv'} = \langle v | \mathbf{d} | v' \rangle \quad (7)$$

for the transition from state v to v' . Since this is a three-dimensional harmonic oscillator, we must consider the x , y , and z components of \mathbf{d} . We will calculate d_i where i can be replaced by x , y , and z . Using the harmonic oscillator raising and lowering operators, we find

$$\begin{aligned} d_{i,vv'} &= \langle v | q\hat{x}_i | v' \rangle \\ &= \sqrt{\frac{\hbar}{2\mu\omega}} \langle v | q(\hat{a}_i + \hat{a}_i^\dagger) | v' \rangle \\ &\propto \sqrt{v'} \langle v | v' - 1 \rangle + \sqrt{v' + 1} \langle v | v' + 1 \rangle. \end{aligned} \quad (8)$$

We see from equation (8) that the dipole moment for all dimensions only is non-zero when $\Delta v = v' - v = \pm 1$. The energy of photons, E_γ , emitted during allowed transitions from $v + 1$ to v is

$$E_\gamma = -(\Delta E) = E_{v+1} - E_v = \hbar\omega_e. \quad (9)$$

Interestingly, we find that the photon energy does not depend on v at all. This tells us that we should observe emitted photons only with energy $\hbar\omega_e$, giving us a single peak in our spectrum. However, this is not what we observe in Figure 1. To understand where all the peaks come from, we must investigate how rotational transitions add to our spectrum.

B. Rotations Modeled as the Rigid Rotor

We approximate the rotations of diatomic molecules by considering two point masses kept a fixed distance apart, r . This model is called the rigid rotor. From classical physics, we know the energy of rotation is $E = J^2/(2I)$ where J is the angular momentum and I is the moment of inertia. In our model, the two rotating point masses with reduced mass μ will have $I = \mu r^2$.

We adapt these equations to arrive at a Hamiltonian for the quantum mechanical rigid rotor, $\hat{H} = \hat{J}^2/(2I)$. The time independent Schrödinger equation is

$$\frac{\hat{J}^2}{2I} |\psi\rangle = E |\psi\rangle \quad (10)$$

We see that the solutions for $|\psi\rangle$ will be spherical harmonics, which are eigenstates of \hat{J}^2 . Thus, the wavefunction for $|\psi\rangle$ is

$$\psi_{JM} = Y_{JM} = \frac{1}{\sqrt{2\pi}} \Theta_{JM}(\theta) e^{iM\phi} \quad (11)$$

where $\Theta_{JM}(\theta) = P_J^M(\cos\theta)$ are Legendre polynomials. It is easy to find the energy levels, which we write as

$$\frac{\hat{J}^2}{2I} |\psi_{JM}\rangle = \frac{\hbar^2 J(J+1)}{2I} |\psi_{JM}\rangle \equiv B J(J+1) |\psi_{JM}\rangle \quad (12)$$

where $B = \hbar^2/(2I)$ has units of energy. The quantum numbers $J = 0, 1, 2, \dots$ and $M = -J, \dots, +J$ indicate that $|\psi_{JM}\rangle$ is an eigenstate of both \hat{J}^2 and \hat{J}_z .

As with vibrational transitions, we can derive the allowed rotational transitions (i.e. the allowed values for ΔM and ΔJ) by calculating the transition dipole moment:

$$\mathbf{d}_{JM;J'M'} = \langle \psi_{J,M} | \mathbf{d} | \psi_{J',M'} \rangle. \quad (13)$$

We can rewrite \mathbf{d} in spherical coordinates as

$$\mathbf{d} = d_0(\sin \theta \cos \phi \mathbf{e}_x + \sin \theta \sin \phi \mathbf{e}_y + \cos \theta \mathbf{e}_z). \quad (14)$$

We use equations (11), (13), and (14) to find the transition dipole moment:

$$\begin{aligned} \mathbf{d}_{JM;J'M'} &= \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \psi_{JM}^* \mathbf{d} \psi_{J'M'} \sin \theta \, d\theta \, d\phi \\ &= \frac{d_0}{2\pi} \left[\mathbf{e}_x \iint e^{i(M'-M)\phi} \Theta_{JM} \sin \theta \cos \phi \Theta_{J'M'} \sin \theta \, d\theta \, d\phi \right. \\ &\quad + \mathbf{e}_y \iint e^{i(M'-M)\phi} \Theta_{JM} \sin \theta \sin \phi \Theta_{J'M'} \sin \theta \, d\theta \, d\phi \\ &\quad \left. + \mathbf{e}_z \iint e^{i(M'-M)\phi} \Theta_{JM} \cos \theta \Theta_{J'M'} \sin \theta \, d\theta \, d\phi \right]. \end{aligned} \quad (15)$$

By evaluating these integrals, we find that they are non-zero only when $\Delta M = 0, \pm 1$ and $\Delta J = \pm 1$; these are the only allowed pure rotational transitions, as shown in Figure 2(A) [3].

Now that we know the allowed energy transitions, we again calculate the energy of photons emitted during these transitions. From equation (12) we see that the energy is dependent only on J , so we don't have to consider how changes in M will affect the energy. The change in energy of rotational transitions from $J + 1$ to J is

$$\begin{aligned} E_\gamma &= -(\Delta E) = E_{J+1} - E_J \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= 2B(J+1). \end{aligned} \quad (16)$$

Unlike with vibrational energy transitions, the energy of an emitted photon is dependent on the starting value of J . We will therefore observe photons with energies equal to $2B(J+1)$. If we plot the energies of detected photons as shown in Figure 2(B), we see that the spacing between peaks is $2B$.

Now we begin to see something closer to the vibration-rotation spectrum shown in Figure 1 with several equally spaced peaks. However, there are still features of Figure 1 that aren't explained, including the gap in the middle where it seems to skip a peak. To explain this, we will examine transitions where both v and J change.

C. Combining Vibrations and Rotations

We will now consider the transitions between vibrational and rotational eigenstates simultaneously. For

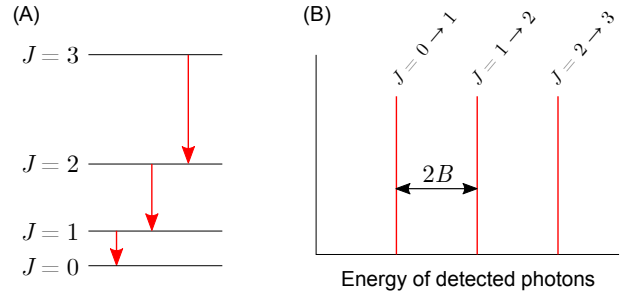


FIG. 2: The diagram in (A) illustrates the rotation energy levels and possible transitions for emission of a photon. A sketch of the corresponding spectrum is shown in (B). The spacing between peaks is equal to $2B$.

convenience, we define the function $G(v)$ to be the contribution to energy from vibrations; similarly $F(J)$ is defined to be the contribution to energy from rotations. Equations (6) and (10) give us

$$\begin{aligned} G(v) &= \hbar\omega_e(v + \frac{1}{2}), & v = 0, 1, 2, \dots \\ F(J) &= BJ(J+1), & J = 0, 1, 2, \dots \end{aligned} \quad (17)$$

First, we want to understand the relative scales of vibrational and rotational transitions. Experimental values for B indicate it is much smaller than typical values for vibrational energy level spacing [3]. Knowing this, we deduce that emission of a photon would require that v decrease but would not restrict J to necessarily decrease. This is illustrated in Figure 3. Thus we consider the energy transitions for $\Delta v = -1$ and $\Delta J = \pm 1$

We note that most physical chemistry textbooks examine the energy transitions for absorption of a photon. However, we will be doing our calculations to find the energy of an emitted photon, since that is what physically happens during a spectroscopy experiment. As a result, some of our signs may be flipped compared to our references (e.g. while it is standard to consider transitions where $\Delta v = +1$, we will look at $\Delta v = -1$).

We can calculate the possible photon energies for transitions with $\Delta v = -1$ and $\Delta J = \pm 1$ just like we did before. The energy of an emitted photon for $\Delta J = +1$ is

$$\begin{aligned} E_{\gamma,+1} &= -(\Delta E) = E_{v,J} - E_{v-1,J+1} \\ &= G(v) + F(J) - G(v-1) - F(J+1) \\ &= \hbar\omega - 2B(J+1) \end{aligned} \quad (18)$$

and for $\Delta J = -1$ is

$$\begin{aligned} E_{\gamma,-1} &= -(\Delta E) = E_{v,J} - E_{v-1,J-1} \\ &= G(v) + F(J) - G(v-1) + F(J-1) \\ &= \hbar\omega + 2BJ. \end{aligned} \quad (19)$$

Like with the pure rotational spectrum shown in Figure 2, we see that the energy of photons for these transitions have a spacing of $2B$. Interestingly, we have no spectral

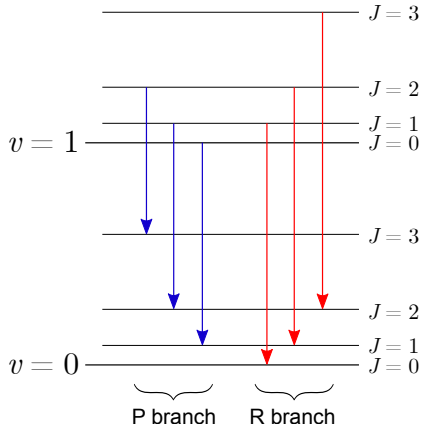


FIG. 3: This illustrates the vibration-rotation energy levels and shows possible transitions for emission of a photon. For the energy to decrease, we must have $\Delta v = -1$, but J can increase or decrease by ± 1 .

peak at exactly $\hbar\omega_e$ as we did when only considering vibrational transitions. This is because there is no transition for $\Delta J = 0$.

There now appear to be two groups of spectral peaks on either side of $\hbar\omega_e$. One group is called the ‘‘P branch’’ and corresponds to $\Delta J = +1$ transitions; the other is called the ‘‘R branch’’ and corresponds to $\Delta J = -1$ transitions. These results closely match the HCl spectrum we saw in Figure 1. An annotated version of the spectrum is shown in Figure 4.

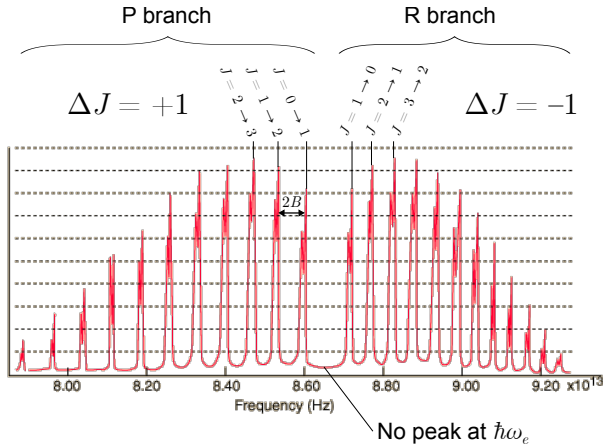


FIG. 4: Here again is the vibration-rotation spectrum of HCl, annotated to show our results in analyzing the vibration-rotation energy transitions.

Notice there are still some aspects of the HCl spectrum that can’t be explained from what we have done so far. For example, the spacing in the P branch is larger than in the R branch. In order to explain this, we will have to find more accurate models for the vibrational and rotational energy eigenstates of a diatomic molecule.

IV. CORRECTIONS TO THE SIMPLE MODELS

There are several adjustments to be made to our models above in order for them to more accurately explain the vibration-rotation spectrum of HCl. We will first discuss the physical motivations for two important corrections – vibration-rotation dependence and centrifugal distortion – and examine how they affect the HCl spectrum. We will then derive them more rigorously in Section IV-C by examining the Dunham potential.

A. Vibration-Rotation Dependence

Our first correction comes from the fact that rotational energy levels depend on the vibrational energy level. We know that the energy levels of the rigid rotor are dependent on the distance between the two atoms. This distance will change as the molecule vibrates with different energies.

This results in a dependence on the vibrational quantum number, v , in $F(J)$ from equation (17). We replace B with

$$B_v \equiv B_e - \alpha_e(v + \frac{1}{2}) \quad (20)$$

where $B_e = \hbar^2/(2I)$ and $\alpha_e = B_e^2/(\hbar\omega_e)$.

By calculating the energy level transitions, we will see that this correction helps to explain the difference in spacing between peaks in the R and P branches. Consider the transition from $v = 1$ to $v = 0$. The $\Delta J = +1$ transition, corresponding to the P branch, will have spectral peaks at

$$\begin{aligned} E_{\gamma,+1} &= -(\Delta E) = E_{1,J} - E_{0,J+1} \\ &= G(1) + F_{v=1}(J) - G(0) - F_{v=0}(J+1) \\ &= \hbar\omega_e - 2B_0 + (B_1 - 3B_0)J + (B_1 - B_0)J^2 \end{aligned} \quad (21)$$

and the $\Delta J = -1$ transition, corresponding to the R branch, will have spectral lines at

$$\begin{aligned} E_{\gamma,-1} &= -(\Delta E) = E_{1,J} - E_{0,J-1} \\ &= G(1) + F_{v=1}(J-1) - G(0) - F_{v=0}(J) \\ &= \hbar\omega_e + (B_1 + B_0)J + (B_1 - B_0)J^2. \end{aligned} \quad (22)$$

When we substitute the expressions for B_1 and B_0 in equation (20), we find

$$\begin{aligned} E_{\gamma,+1} &= \hbar\omega_e - 2B_e + \alpha_e - 2B_eJ - \alpha_eJ^2 \\ E_{\gamma,-1} &= \hbar\omega_e - (2B_e - 2\alpha_e)J - \alpha_eJ^2. \end{aligned} \quad (23)$$

From equation (23) we see that, as J increases, the space between spectral peaks in the P branch ($\Delta J = +1$) is $2B_e$, while the spacing in the R branch ($\Delta J = -1$) is $2B_e - 2\alpha_e$. Thus, the spacing between peaks in the R branch is smaller than in the P branch. This explains the difference in spacing between the branches that we see in the HCl spectrum.

B. Centrifugal Distortion

Our next correction to the simple model also comes from the fact that the bonds of diatomic molecules are not perfectly rigid. The internuclear distance will vary with rotational energy because the centrifugal force will pull the atoms farther apart from each other as the molecule rotates faster. This effect, known as centrifugal distortion, is accounted for by adding a term to $F(J)$:

$$F(J) = BJ(J+1) - D(J(J+1))^2. \quad (24)$$

where D is the *centrifugal distortion constant*, with units of energy. We will describe the derivation of this term in detail in Section IV-C.

We now examine how this affects our HCl spectrum. The energy of a photon emitted due to a pure rotational transition from $J+1$ to J is now

$$E_\gamma = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3. \quad (25)$$

The spacing between peaks is no longer be $2B$, but is instead $2B - 12D - 24DJ - 12DJ^2$. As J gets large, the spacing between peaks will decrease. This effect can be seen in our HCl spectrum when the spacing of peaks near the edges of Figure 1 are examined.

C. The Dunham Potential

Now that we have an idea of what corrections need to be made, we shall delve into the math supporting them. The Dunham potential considers the potential, $V(r)$, of a vibrating and rotating molecule, which varies with the internuclear distance, r . Unlike in Section III-A, we will not approximate the potential as a harmonic oscillator. It is convenient to use a dimensionless variable, $\xi \equiv (r - r_e)/r_e$, where r_e is the equilibrium internuclear distance.

We will consider how this potential fits into a Hamiltonian accounting for both vibrations and rotations. The Schrödinger equation, slightly rearranged, will read

$$\frac{d^2\psi}{d\xi^2} + \frac{2mr_e^2}{\hbar^2} \left(E - V(\xi) - \frac{\hat{J}^2}{2mr_e^2(1+\xi)^2} \right) \psi = 0 \quad (26)$$

where the last term, which is dependent on J , comes from the centrifugal force of rotations [5]; we will define this term to be

$$V_{\text{cent}} = \frac{J(J+1)}{2mr_e^2(1+\xi)^2}. \quad (27)$$

We now expand $V(\xi)$ as a Taylor series about $\xi = 0$ [5]:

$$V(\xi) = V(0) + \left. \frac{dV}{d\xi} \right|_0 \xi + \left. \frac{d^2V}{d\xi^2} \right|_0 \xi^2 + \dots \quad (28)$$

Like in Section III-A, $\left. \frac{dV}{d\xi} \right|_0 = 0$ because $\xi = 0$ is at the minimum of the potential, and we define $V(0)$ to be equal to zero since we only care about relative energies.

To find a more accurate model than before, we consider higher order terms in the expansion of $V(\xi)$. First, we rewrite our expansion of $V(\xi)$ in equation (28) to make constants easier to keep track of:

$$V(\xi) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \dots). \quad (29)$$

Since we want to look at the rotational transitions, we will examine $V_{\text{eff}} = V(\xi) + V_{\text{cent}}(\xi)$. We can expand $V_{\text{cent}}(\xi)$, defined in equation (27), as a Taylor series about $\xi = 0$ so that it matches the form of $V(\xi)$. Combining this with equation (29), we find

$$V_{\text{eff}}(\xi) = a_0\xi^2(1 + a_1\xi + z_2\xi^2 + \dots) + B_e J(J+1)(1 - 2\xi + 3\xi^2 - 4\xi^4 + \dots) \quad (30)$$

where $B_e = \hbar^2/(2I)$ [5].

Now we can use the WKB semiclassical approximation and the quantization condition for a “soft wall” potential to find the energy levels [3]. WKB theory tells us that

$$\frac{\sqrt{2\mu}}{\hbar} \int_{r_1}^{r_2} \sqrt{E - V(r)} dr = (v + \frac{1}{2})\pi \quad (31)$$

where r_1 and r_2 are the classical turning points of $V(r)$ at energy E [2]. In his paper *The Energy Levels of a Rotating Vibrator*, Dunham solves this integral with the potential in equation (30) through a series of Taylor expansions and approximations. This long, but relatively straightforward calculation is discussed further in his paper [5]. He ultimately finds the energy levels to be given by

$$E_{vJ} = \sum_{jk} Y_{jk} (v + \frac{1}{2})^j (J(J+1))^k \quad (32)$$

where Y_{jk} is a constant, different for every j and k . Dunham calculated these constants in terms of a_0, a_1, \dots , then expressed them in terms of common spectroscopy constants.

These results are often written in the following generalized form:

$$F_v(J) = B_v J(J+1) - D_v (J(J+1))^2 + \dots \quad (33)$$

$$G(v) = \hbar\omega_e (v + \frac{1}{2}) - \hbar\omega_e x_e (v + \frac{1}{2})^2 + \dots$$

where

$$B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2 + \dots \quad (34)$$

$$D_v = D_e + \beta_e (v + \frac{1}{2}) + \dots$$

This confirms the claims in equations (20) and (24), and provides new higher order corrections. These higher order corrections correspond to physical phenomena beyond the scope of this paper [1]. With the mathematical support of the Dunham potential, we can feel confident in our understanding of the features of the HCl spectrum.

V. DISCUSSION AND CONCLUSION

From the calculations above, we have successfully achieved an understanding of where the peaks in the HCl spectrum in Figure 1 come from. The spectrum is of a transition from $v = 1$ to $v = 0$, and each peak corresponds to a different transition between rotational energy eigenstates. With this knowledge, we can use the spectrum to explore many interesting molecular properties.

For example, if we can find a value for ω_e , we can find the bond “stiffness”, k by using the formula $\omega_e = (k/\mu)^{1/2}$. We found in Section III-C that the energy corresponding to $\hbar\omega_e$ is halfway between the two peaks closest to the center of the spectrum in Figure 4. If we estimate the positions of those two center peaks to be 8.60×10^{13} Hz and 8.72×10^{13} Hz, we can conclude that $\hbar\omega_e \approx h \cdot (8.66 \times 10^{13} \text{ Hz})$, where h is Planck’s constant, as shown in Figure 5(A). By plugging in the known values for \hbar , h , and the masses of hydrogen and chlorine, we find the bond stiffness to be $k \approx 481 \text{ N}$. Despite our rough estimates, this is quite close to the accepted value for HCl bond stiffness [4].

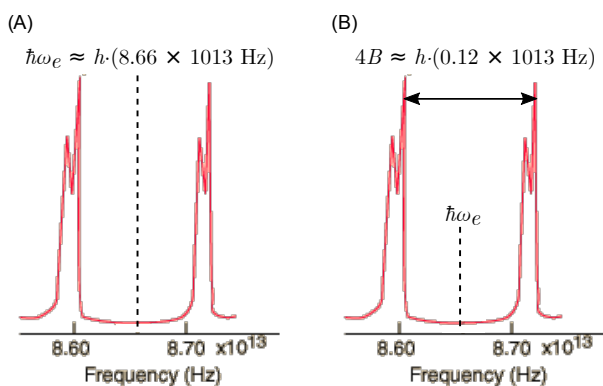


FIG. 5: In (A) we estimated the value of ω_e by estimating the midway point between the two peaks in the HCl spectrum closest to the center. In (B) we estimated B by approximating the space between those two peaks to be $4B$.

Additionally, we can calculate the bond length of HCl from this spectrum. We assume that the spacing between the two peaks shown in Figure 5(B) is approximately equal to $4B$, two times the spacing between rotational

peaks. We know that $B = \hbar^2/(2I) = \hbar^2/(2\mu r^2)$. By plugging in our estimate for B and the known values for \hbar and the masses of hydrogen and chlorine, we can find r , the average bond length. As shown in Figure 5(B), we estimated that $4B \approx h \cdot (0.12 \times 10^{13} \text{ Hz})$. From this we find the bond length, r , to be approximately 0.13 nm [4].

A more accurate way to find the bond length would be to use a pure rotational spectrum like the one illustrated in Figure 2, where the vibrational energy level does not change. In this situation, there are fewer corrections to B that need to be made and we can get a more accurate measure for B and for bond length. Nevertheless, our estimate from the vibration-rotation spectrum comes very close to the value often obtained from a pure rotational spectrum, $r = 0.127 \text{ nm}$ [4].

Of course, there is still more to uncover from our HCl spectrum in Figure 1. We did not discuss the physical meaning behind differences in peak intensities. Additionally, there are effects not directly relevant to the spectrum in Figure 1 that are still important areas of study. For example, one could study vibrational transitions other than $v = 1$ to $v = 0$ and observe effects like vibrational overtones [1].

Finally, one can go beyond diatomic molecules to study the vibration-rotation spectra of polyatomic molecules. Polyatomic molecules have different selection rules, allowing for transitions where $\Delta J = 0$; this gives rise to a “Q branch” which appears in between the P and R branches in the spectrum [3].

Through spectroscopy, we are able to observe scores of properties of diatomic molecules and beyond, giving us a window through which to study their fundamental quantum structures. Spectroscopy allows us to test our models and, as we did in this paper, to use experimental data to correct our models to arrive at ever more precise predictions.

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