Experiment [IRS]: Determining Molecular Constants with Rotational-VibrationalSpectroscopy

Qianrui Li

October 30, 2023

Abstract

The vibrational rotational spectrums of the HCl molecule and cigarette smoke were obtained in this experiment using a Fourier Transform Infrared Spectrometer (FTIR). For the HCl molecule, each peak in the spectrum splited into two peaks because ^{35}Cl had an isotope, ^{37}Cl, which was heavier and had lower transition energy. The rotational constant in the ground vibrational state, B_0, and first existed state, B_1, of HCl^{35} were determined as 10.3488 ±0.0110 cm^{-1} and 10.0456 ±0.0110 cm^{-1} respectively, and were used to calculate the value of B_e, which was 10.5003 ±0.0110 cm^{-1}. The bond length in different vibrational level (r_0, r_1, r_e), the equilibrium oscillation frequency ω_e, anharmonicity constant x_e, zero-point energy G(0), and force constant of HCl^{35} and HCl^{37} were calcualted and compared with the literature value. The difference between the parameters of HCl^{35} and HCl^{37} were disccussed. The spectrum of cigarette smoke was also obtained, and the peaks in the spectrum were assigned to the vibrational rotational transition of CO, CO_2, HCN, CH_4, and H_2O. The values of B_0, B_1, B_e, r_0, r_1, r_e, ω_e, x_e, G(0), and force constant of CO were calculated and compared with the value of HCl, and the difference between them was discussed.

1 Introduction

Vibrational Energy

The vibrational population can be transferred from the ground state to a higher state by absorbing energies. The *fundamental absorption* described the transition from v=0 to v=1, and the energy was usually in the range of 500 cm^{-1} to 4000 cm^{-1}, which was within the infrared region.

The energy levels for diatomic molecules in an anharmonic state could be expressed as shown in equation 1.

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

In the first part of the equation 1 represented the energy of a harmonic oscillator, while the second part was the correction term for an anharmonic oscillator. The energy of an anharmonic oscillator was lower than the energy of a harmonic oscillator with an amount depending on the anharmonic constant $\omega_e x_e$. The frequency of the anharmonic oscillator was shown as ω_e. With equation 1, the ground state energy could be shown as equation 2 with v=0, and so as the first excitation state (v=1) and the second excitation state (v=2).

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e \tag{2a}$$

$$G(1) = \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e \tag{2b}$$

$$G(2) = \frac{5}{2}(\omega_e - \frac{25}{4}\omega_e x_e) \tag{2c}$$

With equation 2, the energy of the fundamental absorption (v=0 to v=1) and the energy of the first overtone (v=0 to v=2) could be calculated as shown in equation 3.

$$G(0 \rightarrow 1) = G(1) - G(0) = \omega_e - 2\omega_e x_e \tag{3a}$$

$$G(0 \rightarrow 2) = G(2) - G(0) = 2(\omega_e - 3\omega_e x_e) \tag{3b}$$

Rotational Energy

The rotational energy could be described using equation 4 for a diatomic molecule.

$$F(J) = B_v(J + 1) \tag{4}$$

In this equation, J was the rotational quantum number, while B_v was the rotational constant, which was related to the moment of inertia I as shown in equation 5.

$$B_v = \frac{h}{8\pi^2 cI} \tag{5a}$$

$$I = \mu r^2 \tag{5b}$$

Transition Energy

Since the vibrational transition and the vibrational transition involved two very different frequencies. The energy for vibrational rotational transition could be expressed as equation 6, while the centrifugal distortion was ignored here.

$$S(v, J) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 \omega_e x_e + B_v(J + 1) \tag{6}$$

The scale of the constant B would change with increasing vibrational state v because the bond length would increase when the molecule vibrates more violently due to the anharmonicity. Since the value of B depended on the bond length, B would be changed in different vibrational state, which could be quantified by the equation 7.

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) \tag{7}$$

In this equation, B_e was the rotational constant for the ground state, while α_e was the anharmonicity constant.

Rotational Selection Rules

When there were two transitions, the rotational state J in the lower vibrational state would be denoted as double prime (J''), while the rotational state J in the upper vibrational state would be denoted as prime (J').

The transition where $\Delta J = 0$ was forbidden, meaning that transition from J''=1 to J'=1 was not allowed. For $\Delta J = 1$ was allowed and would be shown in the spectrum. The P, Q, R branches were defined based on ΔJ:

1. P branch - A transition where ΔJ=-1, for example, J''=1 to J'=0.
2. Q branch - A transition where ΔJ=0, for example, J''=1 to J'=1.
3. R branch - A transition where ΔJ=+1, for example, J''=1 to J'=2.

From equation 6, the energy of any rotational state J'' in the ground vibrational state v=0 and the energy of rotational state J' in v=1 could be deduced as shown in equation 8.

$$S(0, J'') = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + B_0(J + 1) \tag{8a}$$

$$S(1, J') = \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e + B_1(J + 1) \tag{8b}$$

Therefore, the transition energy from J'' to J' could be calculated by subtracting equation 8a from equation 8b as shown in equation 9

$$S(0, J'' \rightarrow 1, J') = \omega_e - 2\omega_e x_e + (B_1 - B_0)(J + 1) \tag{9}$$

In an R-branch, $\Delta J = +1$, so J' = J'' + 1. Therefore, the transition energy for an R-branch could be calculated as shown in equation 10 based on equation 9.In the following equation, J'' was written as J for simplicity.

$$S(R(J)) = \omega_e - 2\omega_e x_e + B_1(J+1)(J+2) - B_0 J(J+1) \tag{10}$$

In a P-branch, $\Delta J = -1$, so J' = J'' - 1. Therefore, the transition energy for an P-branch could be calculated as shown in equation 11 based on equation 9.

$$S(P(J)) = \omega_e - 2\omega_e x_e + B_1 J(J - 1) - B_0 J(J + 1) \tag{11}$$

The rotational constant B_0 and B_1 could be calculated respectively based on equation 10 and 11 as shown in equation 12.

$$S(R(J)) - S(P(J)) = 4B_1(J + 1/2) \tag{12a}$$

$$S(R(J)) - S(P(J + 2)) = 4B_0(J + 3/2) \tag{12b}$$

These equations were linear, and the value of B_0 and B_1 could be obtained by plotting the R(J)-P(J) against (J+1/2) and R(J)-P(J+2) against (J+3/2) respectively. The slope of the plot was four times the rotational constant B_0 and B_1.

2 Methodology

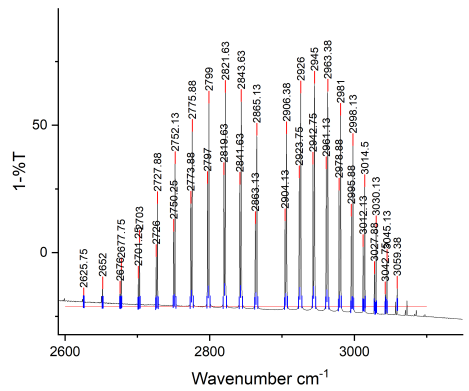
The 10 cm^3 gas cell was flushed with nitrogen and sealed with the Teflon lids. The background scan was performed with this cell using FT-IR spectrometer in the range 6000 cm^{-1} - 2000 cm^{-1} for 64 folds with resolution as 0.5. Three drops of concentrated HCl were added into the cell, and the spectrum was recorded under the same conditions.

The background scan was performed again under the same conditions with a larger gas cell. Cigarette smoke was captured in the cell using a tube to transform. The spectrum of cigarette smoke was recorded under the same conditions.

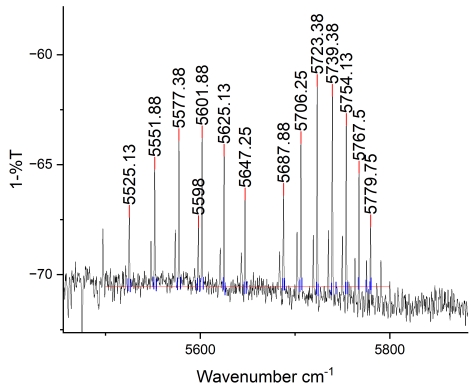
3 Results

The IR sepctrum of HCl was recorded. The fundamental absorption of HCl^{35} was observed at 2885.76 cm^{-1}, while the first overtone was observed at 5667.57 cm^{-1}. The

fundamental absorption of HCl^{37} was observed at 2883.51 cm^{-1}, while the first overtone was observed at 5665.32 cm^{-1}. The spectrum of HCl were shown in Figure 1.



(a) *Fundamental absorption.*



(b) *First overtone.*

Figure 1: *The IR spectrum of HCl. The plot (a) was the fundamental absorption, while (b) was the first overtone.*

Since the P branch had a lower transition energy than the R branch, The peak with lower wavenumber would be P branch, while the peak with larger peak would be the R branch.

The wavenumber of the fundamental absorption for HCl^{35} and HCl^{37} were recorded separately in Table 1 and Table 2. The value of R(J)-P(J) and R(J)-P(J+2) were calculated to determine the rotational constant B_0 and B_1 for HCl^{35} and HCl^{37} respectively as shwon in Table 1 and Table 2.

Table 1: *The wavenumber of the fundamental absorption for HCl^{35} in P branch and R branch.*

J	P (cm^{-1})	R (cm^{-1})	R(J)-P(J) (cm^{-1})	R(J)-P(J+2) (cm^{-1})
0	-	2906.38	-	62.75
1	2865.13	2926.00	60.87	104.37
2	2843.63	2945.00	101.37	146.00
3	2821.63	2963.38	141.75	187.50
4	2799.00	2981.00	182.00	228.87
5	2775.88	2998.13	222.25	270.25
6	2752.13	3014.50	262.37	311.50
7	2727.88	3030.13	302.25	352.38
8	2703.00	3045.13	342.13	-
9	2677.75	-	-	-

Table 2: *The wavenumber of the fundamental absorption for HCl^{37} in P branch and R branch.*

J	P (cm^{-1})	R (cm^{-1})	R(J)-P(J) (cm^{-1})	R(J)-P(J+2) (cm^{-1})
0	-	2904.13	-	62.50
1	2863.13	2923.75	60.62	104.12
2	2841.63	2942.75	101.12	145.75
3	2819.63	2961.13	141.50	187.25
4	2797.00	2978.88	181.88	228.63
5	2773.88	2995.88	222.00	269.88
6	2750.25	3012.13	261.88	310.88
7	2726.00	3027.88	301.88	351.88
8	2701.25	3042.75	341.50	-
9	2676.00	-	-	-

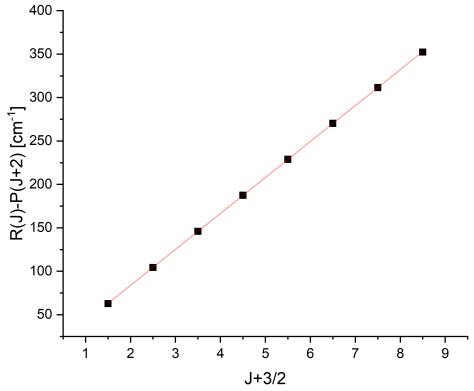
The rotational constant B_0 could be obtained by plotting the R(J)-P(J) against (J+1/2) based on equation 12(a) as shown in Figure 2(a) for HCl^{35}. The rotational constant B_1 could be obtained by plotting the R(J)-P(J+2) against (J+3/2) based on equation 12(b)as shown in Figure 2(b) for HCl^{35}.

The slope in Figure 2(a) was was four times the rotational constant B_0, which was calculated as shown in equation 13.

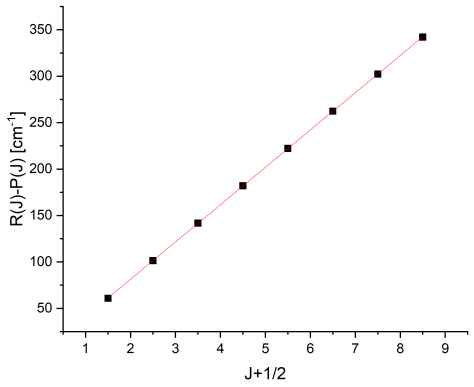
$$B_0 = \frac{41.3950 \pm 0.0442}{4} = 10.3488 \pm 0.0110 cm^{-1} \quad (13)$$

The slope in Figure 2(b) was four times the rotational constant B_1, which was calculated as shown in equation 14.

$$B_1 = \frac{40.1825 \pm 0.0440}{4} = 10.0456 \pm 0.0110 cm^{-1} \quad (14)$$



(a) *R(J)-P(J+2) was plotted against (J+3/2).*



(b) *R(J)-P(J) was plotted against (J+1/2).*

Figure 2: *The rotational constant B_0 and B_1 for HCl^{35} were calculated based on the slope of the plot. The slope of plot (a) was 41.3950 ±0.0442 with $r^2 = 1$, which was four times the rotational constant B_0. The slope of plot (b) was 40.1825 ±0.0440 with $r^2 = 0.99$, which was four times the rotational constant B_1.*

The rotational constant at equation, B_e, could be calculated based on B_0 and B_1 as shown in equation 15 based on equation 7.

$$10.3488 = B_e - \alpha_e(0 + 1/2) \tag{15a}$$
$$10.0456 = B_e - \alpha_e(1 + 1/2) \tag{15b}$$

The value of B_e was determined by solving these two equations, which was 10.5003 ±0.0110 cm^{-1}. The value of α_e was also obtained as 0.3029 cm^{-1}.

The bond length of HCl in different vibrational could be caluclated using B_0, B_1, and B_e based on equation 5 respectively as shown in equation 16.

$$\mu = \frac{m_H m_{^{35}Cl}}{m_H + m_{^{35}Cl}} = 1.6266 \times 10^{-27} kg \tag{16a}$$
$$r_0 = \sqrt{(\frac{h}{8\pi^2 \mu B_0 c})} = 129.0pm \tag{16b}$$
$$r_1 = \sqrt{(\frac{h}{8\pi^2 \mu B_1 c})} = 130.9pm \tag{16c}$$
$$r_e = \sqrt{(\frac{h}{8\pi^2 \mu B_e c})} = 128.0pm \tag{16d}$$

The equilibrium oscillator frequency ω_e and the anharmonic constant $x_e$could be calculated based on the energy of the fundamental absorption and the first overtone as shown in equation 3. The frequency of the fundamental absorption was 2885.76 cm^{-1}, while the frequency of the first overtone was 5667.57 cm^{-1}. The value of ω_e and x_e were calculated as shown in equation 17.

$$2885.76 = \omega_e - 2\omega_e x_e \tag{17a}$$
$$5667.57 = 2(\omega_e - 3\omega_e x_e) \tag{17b}$$
$$\omega_e = 2989.70cm^{-1} \tag{17c}$$
$$\omega_e x_e = 51.9725cm^{-1} \tag{17d}$$
$$x_e = 0.0017384 \tag{17e}$$

The zero point energy of HCl^{35} could be calcualted using equation 2(a) with the value of ω_e and x_e as shown in equation 18.

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e = 1494.86cm^{-1} \tag{18}$$

The force constant of HCl^{35} bond could be calculated as shown in equation 19 and the reduced mass (μ) of HCl^{35} was calculated as 1.6273×10^{-25}.

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{19a}$$
$$v = c/\lambda = c \times wavenumber \tag{19b}$$
$$v = 2.99792 \times 10^{10} cm \cdot s^{-1} * 2885.76cm^{-1} = 8.65128 \times 10^{13} Hz \tag{19c}$$
$$k = \mu v^2 (2\pi)^2 = 480.618 Nm^{-1} \tag{19d}$$

The value of B_0, B_1, B_e,α_e, r_0, r_1, r_e, ω_e, x_e, $G(0)$, and k for HCl^{35} were summaried in Table 3 and for HCl^{37} were calculated using the same method as shown in Table 3 and 4. This value was compared with the literature value.

Table 3: *The value of B_0, B_1, B_e,α_e, r_0, r_1, r_e, ω_e, x_e, $G(0)$, and k for HCl^{35}.*

	HCl^{35}	Literature value	Error (%)
B_0 (cm^{-1})	10.3488 ±0.0110	10.4404 [1]	0.9
B_1 (cm^{-1})	10.0456 ±0.0110	10.1366 [1]	0.9
B_e (cm^{-1})	10.5003 ±0.0110	10.5923 [1]	0.9
α_e (cm^{-1})	0.3029	0.3038 [1]	0.3
r_0 (pm)	129.0	-	-
r_1 (pm)	130.9	-	-
r_e (pm)	128.0	127.46 [2]	0.4
ω_e (cm^{-1})	2989.70	2990.95 [2]	0.04
x_e	0.017384	0.017659 [2]	1.6
$G(0)$ (cm^{-1})	1494.86	-	-
k (Nm^{-1})	480.619	480.45 [2]	0.04

Table 4: *The value of B_0, B_1, B_e,α_e, r_0, r_1, r_e, ω_e, x_e, $G(0)$, and k for HCl^{37}.*

	HCl^{37}	Literature value	Error (%)
B_0 (cm^{-1})	10.3370 ±0.0130	10.4247 [1]	0.8
B_1 (cm^{-1})	10.0334 ±0.0144	10.1214 [1]	0.9
B_e (cm^{-1})	10.4888 ±0.0137	10.5764 [1]	0.8
α_e (cm^{-1})	0.3036	0.3033 [1]	0.1
r_0 (pm)	128.9	-	-
r_1 (pm)	130.9	-	-
r_e (pm)	128.0	-	-
ω_e (cm^{-1})	2987.39	-	-
x_e	0.017366	-	-
$G(0)$ (cm^{-1})	1480.73	-	-
k (Nm^{-1})	480.6489	-	-

The IR spectrum of the cigarette was recorded, and part of the spectrum from 2000 cm^{-1} to 4000 cm^{-1} was shown in Figure 3.

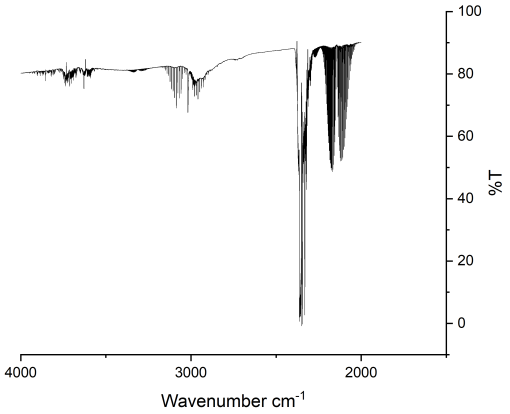


Figure 3: *The IR spectrum of the cigarette.*

The peaks were compared to the literature values and different gases in the cigarette were identified. The peak at 2143.32 cm^{-1} was identified as the fundamental absorption of CO as shown in Figure 4.

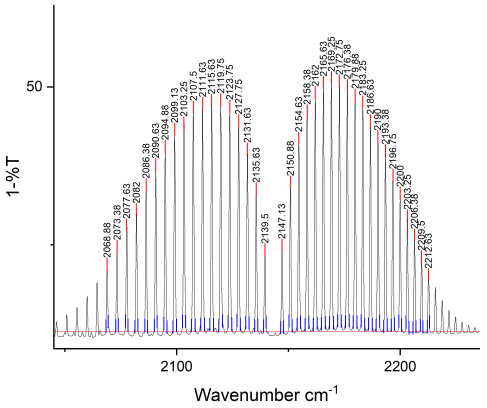


Figure 4: *The IR spectrum of the fundamental absorption of CO.*

The wavenumber of the fundamental absorption of the P-branch and R-branch for CO was recorded, and the value of R(J)-P(J) was calculated as shown in Table 5.

Table 5: *The wavenumber of the fundamental absorption for HCl^{37} in P branch and R branch.*

J	P (cm^{-1})	R (cm^{-1})	R(J)-P(J) (cm^{-1})	R(J)-P(J+2) (cm^{-1})
0	-	2147.13	-	11.50
1	2139.50	2150.88	11.38	19.25
2	2135.63	2154.63	19.00	26.88
3	2131.63	2158.38	26.75	34.63
4	2127.75	2162.00	34.25	42.25
5	2123.75	2165.63	41.88	50.00
6	2119.75	2169.25	49.50	57.62
7	2115.63	2172.75	57.12	65.25
8	2111.63	2176.38	64.75	73.13
9	2107.50	2179.88	72.38	80.75
10	2103.25	2183.25	80.00	-
11	2099.13	-	-	-

The peak at 4259.94 cm^{-1} was identified as the first overtone of CO as shown in Figure 5.

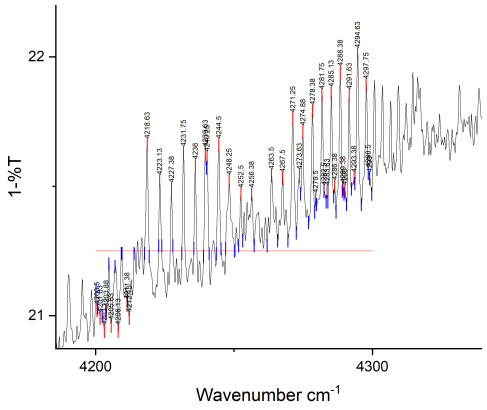


Figure 5: *The IR sepctrum of the first overtone of CO.*

The value of B_0, B_1, B_e,α_e, r_0, r_1, r_e, ω_e, x_e, $G(0)$, and k for CO were calculated using the same method as shown above, and the values were recorde and compared with the literature value as shown in Table 6.

Table 6: *The value of B_0, B_1, B_e,α_e, r_0,r_1, r_e, ω_e, x_e, $G(0)$, and k for CO.*

	Experimental data	Literature value	Error (%)
B_0 (cm^{-1})	1.9227	1.9293[3]	0.3
B_1 (cm^{-1})	1.9053	1.9060[3]	0.04
B_e (cm^{-1})	1.9314	1.9381[3]	0.3
α_e (cm^{-1})	0.01744	0.017507[4]	0.4
r_0 (pm)	113.3	113.03[3]	0.2
r_1 (pm)	113.8	113.55[3]	0.2
r_e (pm)	113.0	-	-
ω_e (cm^{-1})	2170.01	2169.8232[4]	0.008
$\omega_e x_e$	13.3450	13.2932[4]	0.4
x_e	0.0061497	-	-
$G(0)$ (cm^{-1})	1081.67	-	-
k (Nm^{-1})	1856.87	1860[2]	0.2

4 Discussion

In this experiment, the vibrational-rotational spectrum of HCl and cigarette were obtained and analysed. The spectrum was recorded from 2000 cm^{-1} to 6000 cm^{-1} because the fundamental absorbing for a diatomic molecule was from 2000 cm^{-1} to 4000 cm^{-1}, while the first overtone of a diatomic molecule was from 4000 cm^{-1} to 6000 cm^{-1}. The resolution of the spectrometer was set to be 0.5, which was the highest value and would give a clear structure of the rotational spectrum as the energy absorbed for the rotational transition was small and could only be obtained if the resolution was high enough.

The spectrums were obtained in a gas phase rather than a solution phase because the vibrational-rotational spectrum of a molecule in the gas phase was more clear and easier to analyse due to the high resolution. This was because the molecule in the gas phase would have more degree of freedom compared to the molecule in the solution phase. The molecules in the solution phase would have more interactions with the solvent molecules and were closer to each other, which results in less degree of freedom and low resolution.

Before measuring HCl and cigarette gas, nitrogen was used as a background scan. This was because nitrogen was a diatomic molecule without a dipole moment when vibrating, meaning that it would not absorb any energy in the infrared region due to symmetry. Thus, nitrogen would not shown in the IR spectrum and would not affect the analysis of the sample. Besides, nitrogen was a relatively inert gas, which would not react with the sample. Therefore, nitrogen was an ideal gas for the background scan in this experiment.

In the IR spectrum of HCl, each large peak of the fundamental absorption for HCl was followed by a smaller peak as shown in Figure 1. This was because Cl had an isotope ^{37}Cl with an abundance 24.23%, while ^{35}Cl had an abundance as 75.77%. Since ^{37} Cl was heavier than ^{35}Cl, the reduced mass of HCl^{37} was greater than the reduced mass of HCl^{35}. Therefore, the rotational constant (B) of HCl^{37} would be lower than the rotational constant of HCl^{35} because B was dependent on the reduced mass of the molecule based on equation 5. The energy absorption of HCl^{37} would be lower than the energy absorption of HCl^{35} based on equation 6. Therefore, the split peak with a smaller wavenumber would be the vibrational-rotational spectrum of HCl^{37}, while the split peak with a larger wavenumber would be the vibrational-rotational spectrum of HCl^{35}.

The bond length of HCl^{37} and HCl^{35} were almost the same becaue ^{37}Cl was an isotope of ^{35}Cl, meaning that the chemical properties of ^{37}Cl and ^{35}Cl were similar.

The equilibrium oscillation frequency, ω_e, of HCl^{37} was smaller than the equilibrium oscillation frequency of HCl^{35} because ^{37}Cl was heavier than ^{35}Cl, resulting in slower vibration. This resulted in the smaller value of zero-point energy of HCl^{37} than the zero-point energy of HCl^{35} because the zero-point energy was dependent on the equilibrium oscillation frequency based on equation 2(a).

The force constant of HCl^{37} was slightly greater than the force constant of HCl^{35} because the reduced mass of HCl^{37} was greater than the reduced mass of HCl^{35}, resulting in greater force constant based on equation 19.

In the spectrum of cigarettes, each peak was identified as different gases in the cigarette and compared to the literature value as shown in Table 7.

Table 7: *The wavenumber of gases in the cigarette measured in the experiment and the literature value.*

Gas	Experimental Data (cm^{-1})	Literature value (cm^{-1})	Error (%)
CO	2143.3	2143.7[5]	0.03
CO_2	2349.6	2349.3[5]	0.01
CH_4	3017.6	3020.3[5]	0.09
HCN	3313.19	3311.5[5]	0.05
H_2O	3613.7	-	-

The experimental data was close to the literature value with a small error, which indicated that the experimental data was accurate.

The rotational constant B_v of CO was much smaller than the rotational constant of HCl. For a CO molecule, the difference between carbon and oxygen was small, meaning that the rotational center of the molecule would be close to the middle point of the two molecules. However, for an HCl molecule, the mass of chlorine was much larger than the mass of hydrogen, indicating that the rotational center of the molecule would be very close to chlorine. When the HCl molecule rotated, the chlorine atom would be almost static, while the hydrogen would rotate around the chlorine atom. The reduced mass of CO was much greater than the reduced mass of HCl. This resulted in the smaller rotational constant of CO than the rotational constant of HCl as the rotational constant depended on the reduced mass of the molecule based on equation 5.

The bond length of the HCl was larger than the bond length of CO. This was because the bond length of a diatomic molecule was mainly dependent on the atomic radius of the two atoms. The atomic radius of chlorine was much larger than the atomic radius of oxygen and carbon because chlorine was in the third period and had one more electron shell filled with electrons, while oxygen and carbon were in the second period. Thus, the bond length of HCl would be greater than the bond length of CO.

The equilibrium oscillation frequency, ω_e, of CO was smaller than the equilibrium oscillation frequency of HCl because hydrogen was much lighter than carbon and oxygen, resulting in faster vibration.

Since the value of ω_e of CO was smaller than the value of ω_e of HCl, the zero-point energy of CO was smaller than the zero-point energy of HCl based on equation 2(a).

The force constant of CO was much larger than the force constant of HCl because the reduced mass of CO was greater than the reduced mass of HCl, resulting in a larger force constant based on equation 19.

The calculated parameters for HCl^{35}, HCl^{37}, and CO were compared with the literature value as shown in Tables 3, 4, and 6. The error for each parameter was very small, which indicated that the experimental data was accurate. This might be due to the high resolution of the spectrum, which could give a clear structure of the spectrum and make the analysis of the spectrum more accurate.

In this experiment, one possible experimental error might be that the sample was not fully evaporated, which would lead to a lower resolution and might affect the analysis of the spectrum. This could be improved by increasing the time for waiting before starting to record the spectrum to ensure that the sample was fully evaporated. Another possible error would be that air might be introduced into the sample, and some molecules in the air might also shown in the spectrum which would affect the analysis of the spectrum. To limit the air introduced into the sample, the speed of adding the sample into the cell could be faster. During the recording of the spectrum for cigarettes, the sample might leak out of the sample cell, which would lead to a lower resolution, and gases with low concentrations might not be shown in the spectrum. This could be improved by ensuring that the sample was fully sealed before recording the spectrum.

This experimental setup could be used in industrial

applications to identify the impurities in a sample as the vibrational-rotational spectrum of each molecule was unique. The spectrum could also be used to monitor the reaction process as the vibrational-rotational spectrum of the reactants and products were different. Therefore, the concentration of the reactants and products could be calculated respectively through the spectrum, which could reveal the reaction process.

In this experiment, the vibrational-rotational spectrum of HCl and cigarette were obtained and analysed. The vibrational-rotational spectrum of HCl was split into two peaks due to the different isotopes of chlorine. The fundamental absorption of HCl^{35} was 2885.76 cm^{-1}, while the fundamental absorption of HCl^{37} was 2883.63 cm^{-1}. The first overtone of HCl^{35} was 5663.50 cm^{-1}, while the first overtone of HCl^{37} was 5667.57 cm^{-1}. The value of B_0, B_1, B_e, α_e, r_0, r_1, r_e, ω_e, x_e, $G(0)$, and k for HCl^{35} and HCl^{37} were calculated and compared with the literature value. The vibrational-rotational spectrum of the cigarette was analysed and the gases in the cigarette were identified as CO, CO_2, CH_4, HCN, and H_2O. The wavenumber of each gas was compared to the literature value. The vibrational-rotational spectrum of CO was also analysed and the value of $B_0, B_1, B_e, \alpha_e, r_0, r_1, r_e, \omega_e, x_e, G(0)$, and k for CO were calculated and compared with the literature value. The differences and trends of the parameters were discussed. The error for each parameter was very small, which indicated that the experimental data was accurate.

5 Investigation Question

In the industrial, FTIR could give information about complete and incomplete combustion, which would be discussed below.

During the complete combustion, the fuel would be fully oxidized to carbon dioxide and water as shown in equation 20.

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{20}$$

The fuel usually not only contained carbon and hydrogen, but also contained other elements such as nitrogen, sulfur, and oxygen. Thus, nitrogen dioxide might also be produced during the complete combustion.[6].

If the combustion was incomplete, carbon monoxide would be produced instead of carbon dioxide, and other nitrogen oxides (NO_x) might also exist.[6] Methane was also an important product during the incomplete combustion as shown in the equation.[7]

The sample after combustion could be analysed using FTIR. The representative peaks in the spectrum could be identified as compared to the literature value. The peak from 2200 cm^{-1} to 2400 cm^{-1} represented carbon dioxide, while the peak from 2000 cm^{-1} to 2200 cm^{-1} represented carbon monoxide. Peaks from 2300 cm^{-1} to 3000 cm^{-1} could be assigned to aliphatic carbons.[8] The fundamental absorption of OH strech for H_2O was around 3500 cm^{-1}.[9] The peak around 3020.3 cm^{-1} was correspond to CH_4.[5]

The main difference between complete and incomplete combustion was the production of carbon dioxide or carbon monoxide. Therefore, the analysis could focus on the amount of carbon dioxide and carbon monoxide. The concentration of the gases could be determined using the peak area of the fundamental absorption based on the Beer-Lambert law as shown in equation 21.[10]

$$A = \epsilon cl \tag{21}$$

The ratio of carbon dioxide and carbon monoxide could be calculated by knowing the concentration of both gases, which could be used to determine whether the combustion was complete or incomplete.

This experiment could reveal the concentration of carbon dioxide, which was the main product of complete combustion, and carbon monoxide, which was the main product of incomplete combustion. Thus, it could monitor the process of combustion. The combustion would tend to be complete if the temperature increased. Therefore, this experiment could also be used to determine at which temperature the combustion was fully complete.[8] However, if there were too many gases in the sample, the spectrum might be too complicated to analyse. Besides, this experiment could only measure gas but not liquid or solid, and also the gas without dipole moment would not shown in the spectrum as well. However, during incomplete combustion, carbon might also form, which could not be shown in the spectrum. Therefore, this experiment could only be used to measure the gas with dipole moment. The carbon dioxide might also be produced during incomplete combustion, which might be difficult to analyse.

To improve the reliability of the results, TGA-FTIR could be used.[11] Another method called PCFC-FTIR was also an alternative method to improve the reliability of the results.[7]

References

[1] E. D. T. Earle K. Plyler, *Z. Elektrochem. angew. phys. Chem.*, 1960, **64**, 717–720.

[2] G. Herzberg, *Molecular Spectra and Molecular Structure — I Spectra of Diatomic Molecules*, D.vanNostrand, New York, 2nd edn., 1950.

[3] N. Mina-Camilde, C. Manzanares I. and J. F. Caballero, *Journal of Chemical Education*, 1996, **73**, 804.

[4] D. Rank, A. Pierre and T. Wiggins, *Journal of Molecular Spectroscopy*, 1965, **18**, 418–427.

[5] A. R. Ford, W. A. Burns and S. W. Reeve, *Journal of Chemical Education*, 2004, **81**, 865.

[6] I. Oluwoye, M. Altarawneh, J. Gore and B. Z. Dlugogorski, *Fuel*, 2020, **274**, 117805.
[7] R. Sonnier, G. Dorez, H. Vahabi, C. Longuet and L. Ferry, *Combustion and Flame*, 2014, **161**, 1398–1407.
[8] A. Decimus, R. Sonnier, P. Zavaleta, S. Suard and L. Ferry, *JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY*, 2019, **138**, 753–763.
[9] I. M. Mcintosh, A. R. Nichols, K. Tani and E. W. Llewellin, *American Mineralogist*, 2017, **102**, 1677–1689.
[10] M. R. Roussel, *A Life Scientist's Guide to Physical Chemistry*, Cambridge University Press, Cambridge, 1st edn., 2012.
[11] C. A. Wilkie, *Polymer Degradation and Stability*, 1999, **66**, 301–306.