

Rotational-Vibrational Spectroscopy of Simple Gaseous Diatomeric Molecules

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Spectra

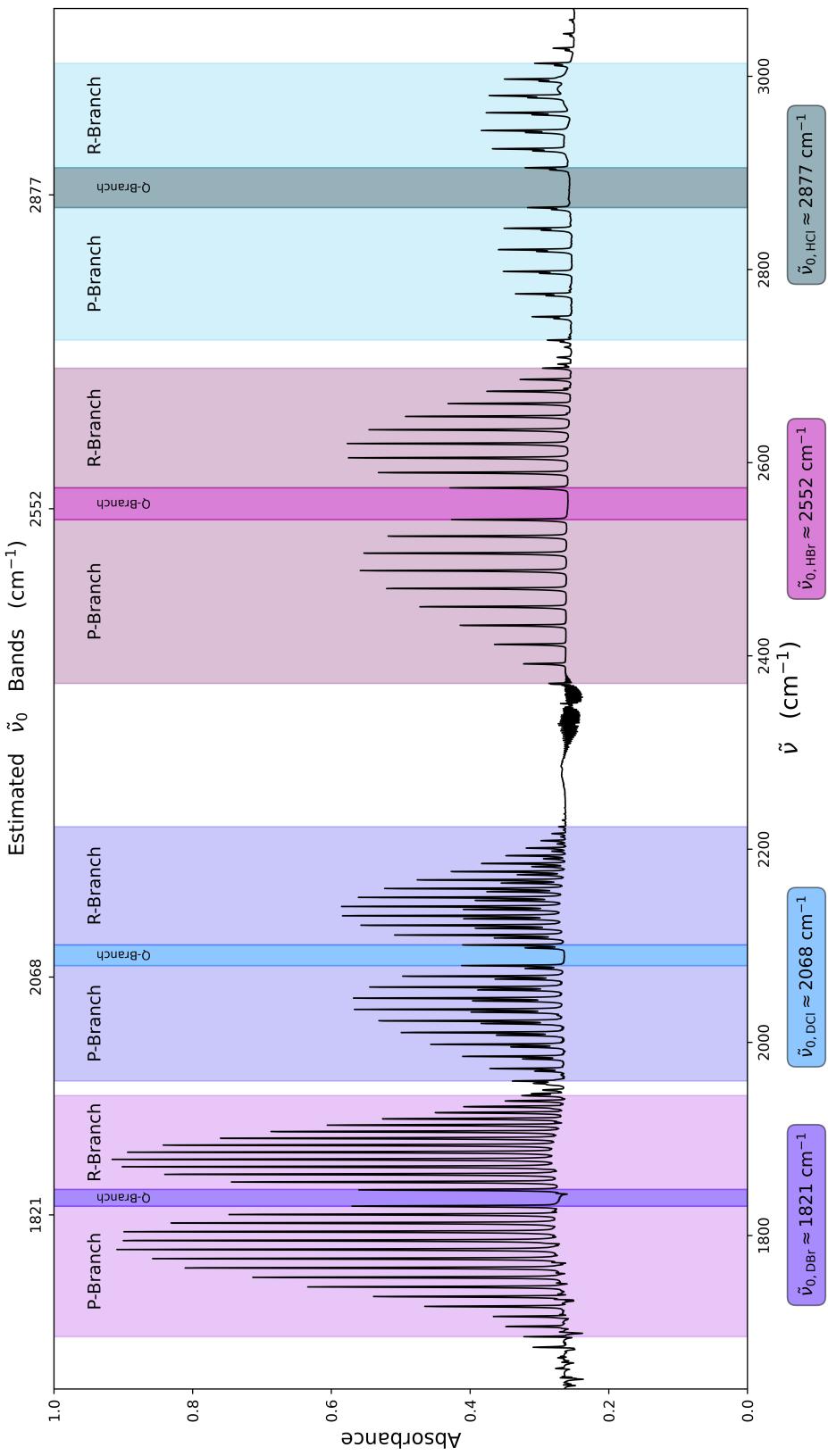


Figure 1: Species A: HCl , Species B: HBr , Species C: DCI , Species D: DBr

Fundamental Frequency

The fundamental frequency, f_0 , for DBr is given by:

$$\begin{aligned}f_{0,DBr} &= \left(\frac{1}{2\pi}\right) \sqrt{\frac{k}{\mu_{DBr}}} \\&= \left(\frac{1}{2\pi}\right) \sqrt{\frac{384 \text{ N/m}}{(79.9040 \text{ amu})(2.0141 \text{ amu})}} \times (79.9040 \text{ amu} + 2.0141 \text{ amu}) \\&= 5.46042386 \times 10^{13} \text{ Hz} \\&\approx \mathbf{54.6 \text{ THz} = 1821 \text{ cm}^{-1}}\end{aligned}$$

Peak Splitting

The energy for the n^{th} vibrational mode is given by $E(v) = hf_0(n + \frac{1}{2})$ where $n = 0, 1, 2, 3, \dots$ is the vibrational quantum number and $f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ is the fundamental vibrational frequency. The energy for the J^{th} rotational mode is given by $E(J) = hcBJ(J+1)$ where $J = 0, 1, 2, 3, \dots$ is the quantum rotational number, $B = \frac{h}{8\pi^2 c I}$ is the rotational constant, and $I = \mu r_e^2$ is the moment of inertia. Under the Born-Oppenheimer approximation, the wavefunctions of the nucleus and electrons are considered distinct. This is due to the electrons being substantially smaller in mass than the nucleus (and therefore having a substantially higher angular frequency) which means we can more or less assume the nucleus is stationary with respect to its electrons. Therefore, we assume changes in electron energy are only from electronic, vibrational, and rotational factors. A very simple model of simple diatomic molecules may be constructed where the total change in observed energy at a fixed electronic energy level is the sum of the vibrational and rotational energies. Since both the vibrational and rotational energies are dependent on the reduced mass of the system, $\mu = \frac{m_1 m_2}{m_1 + m_2}$, the overall energy of a transition will be dependent on μ .

The transitions in the spectrum for HCl and DCI show doublets, indicating two different energies are associated for the HCl and DCI rotational transitions. This can be explained when we consider the two most common chlorine isotopes, ^{35}Cl and ^{37}Cl with relative abundances of $\sim 75\%$ and $\sim 25\%$ respectively (matching the observed splitting ratio of 3:1). The two most common isotopes of bromine are ^{79}Br and ^{81}Br ($\sim 51\%$ and $\sim 49\%$ respectively) which leads to the assumption that the bromine spectra would split at a 1:1 ratio. However, we do not observe any splitting in the bromine lines.

We can explain this by looking at the relative difference in μ between the isotopes of the species. The reduced masses for $H^{35}\text{Cl}$, $H^{79}\text{Br}$, $D^{35}\text{Cl}$, and $D^{79}\text{Br}$ are $\mu_{H^{35}\text{Cl}} \approx 0.9797 \text{ amu}$, $\mu_{H^{79}\text{Br}} \approx 0.9952 \text{ amu}$, $\mu_{D^{35}\text{Cl}} \approx 1.9010 \text{ amu}$, and $\mu_{D^{79}\text{Br}} \approx 1.9639 \text{ amu}$. The reduced masses for $H^{37}\text{Cl}$, $H^{81}\text{Br}$, $D^{37}\text{Cl}$, and $D^{81}\text{Br}$ are $\mu_{H^{37}\text{Cl}} \approx 0.9812 \text{ amu}$, $\mu_{H^{81}\text{Br}} \approx 0.9955 \text{ amu}$, $\mu_{D^{37}\text{Cl}} \approx 1.9099 \text{ amu}$, and $\mu_{D^{81}\text{Br}} \approx 1.9651 \text{ amu}$.

When compared, we see that the reduced masses of $H^{35}\text{Cl}$ is $\sim 0.15\%$ smaller than $H^{37}\text{Cl}$, and that of $D^{35}\text{Cl}$ is $\sim 0.030\%$ smaller than $D^{37}\text{Cl}$. On the other hand, the reduced mass of $H^{79}\text{Br}$ is only $\sim 0.061\%$ smaller than $H^{81}\text{Br}$, whereas that of $D^{79}\text{Br}$ is only $\sim 0.030\%$ smaller than $D^{81}\text{Br}$. This suggests that splitting exists in bromine, but because the relative change in mass is so small the resulting peaks are too close together to resolve, whereas in chlorine the difference is large enough to result in differentiable bands leading to the splitting pattern in its spectra.

Rotational Transitions

Table 1: Rotational Transitions for DBr

Branch	$\tilde{\nu}$ (cm^{-1})	Abs.	J_i	J_f
P-Branch	1695.48047	0.49287	15	14
P-Branch	1705.93066	0.54563	14	13
P-Branch	1716.38086	0.57693	13	12
P-Branch	1726.83105	0.57522	12	11
P-Branch	1737.02636	0.53206	11	10
P-Branch	1746.96679	0.42879	10	9
P-Branch	1756.90722	0.33888	9	8
P-Branch	1766.59277	0.37125	8	7
P-Branch	1776.27832	0.41061	7	6
P-Branch	1785.70898	0.45668	6	5
P-Branch	1794.88476	0.4991	5	4
P-Branch	1804.06054	0.53141	4	3
P-Branch	1813.23632	0.56661	3	2
P-Branch	1821.90234	0.56802	2	1
P-Branch	1830.56836	0.54466	1	0
R-Branch	1847.90039	0.4971	0	1
R-Branch	1855.54687	0.41204	1	2
R-Branch	1863.44824	0.27222	2	3
R-Branch	1871.34961	0.28195	3	4
R-Branch	1878.99609	0.29763	4	5
R-Branch	1886.38769	0.31897	5	6
R-Branch	1893.77929	0.34817	6	7
R-Branch	1900.91601	0.38331	7	8
R-Branch	1907.79785	0.42709	8	9
R-Branch	1914.4248	0.47608	9	10
R-Branch	1921.05175	0.52298	10	11
R-Branch	1927.42382	0.56092	11	12
R-Branch	1933.54101	0.58517	12	13
R-Branch	1939.40332	0.58385	13	14
R-Branch	1945.01074	0.5573	14	15

Table 2: Rotational Transitions for DCI

Branch	$\tilde{\nu}$ (cm^{-1})	Abs.	J_i	J_f
P-Branch	1960.04882	0.41422	11	10
P-Branch	1973.04785	0.47226	10	9
P-Branch	1985.53711	0.52025	9	8
P-Branch	1998.02636	0.55819	8	7
P-Branch	2010.26074	0.55305	7	6
P-Branch	2022.49511	0.51809	6	5
P-Branch	2034.21972	0.42659	5	4
P-Branch	2045.94433	0.29537	4	3
P-Branch	2057.41406	0.32779	3	2
P-Branch	2068.6289	0.37569	2	1
P-Branch	2079.58886	0.43162	1	0
R-Branch	2100.99902	0.50871	0	1
R-Branch	2111.19433	0.4106	1	2
R-Branch	2121.38965	0.32223	2	3
R-Branch	2131.07519	0.34832	3	4
R-Branch	2140.76074	0.36626	4	5
R-Branch	2150.1914	0.46512	5	6
R-Branch	2159.36718	0.53905	6	7
R-Branch	2168.28808	0.63392	7	8
R-Branch	2176.9541	0.71318	8	9
R-Branch	2185.11035	0.81072	9	10
R-Branch	2193.2666	0.85761	10	11
R-Branch	2201.16797	0.9091	11	12
R-Branch	2208.81445	0.89994	12	13
R-Branch	2216.20605	0.89895	13	14
R-Branch	2223.34277	0.83108	14	15

Table 3: Rotational Transitions for HBr

Branch	$\tilde{\nu}$ (cm^{-1})	Abs.	J_i	J_f
P-Branch	2371.68457	0.30671	10	9
P-Branch	2391.82031	0.35042	9	8
P-Branch	2411.95605	0.37233	8	7
P-Branch	2431.83691	0.37666	7	6
P-Branch	2450.95312	0.38368	6	5
P-Branch	2469.81445	0.36769	5	4
P-Branch	2488.4209	0.32051	4	3
P-Branch	2506.51757	0.28632	3	2
P-Branch	2524.10449	0.32267	2	1
P-Branch	2541.18164	0.36468	1	0
R-Branch	2574.06152	0.74744	0	1
R-Branch	2589.86425	0.57012	1	2
R-Branch	2605.15722	0.32528	2	3
R-Branch	2619.94043	0.34923	3	4
R-Branch	2634.21386	0.40899	4	5
R-Branch	2647.97754	0.4501	5	6
R-Branch	2661.23144	0.52606	6	7
R-Branch	2673.97558	0.60582	7	8
R-Branch	2686.20996	0.68695	8	9
R-Branch	2697.93457	0.75986	9	10

Table 4: Rotational Transitions for HCl

Branch	$\tilde{\nu}$ (cm^{-1})	Abs.	J_i	J_f
P-Branch	2726.99121	0.28859	7	6
P-Branch	2751.20507	0.31044	6	5
P-Branch	2774.90918	0.33444	5	4
P-Branch	2798.10351	0.35194	4	3
P-Branch	2820.5332	0.35902	3	2
P-Branch	2842.708	0.35084	2	1
P-Branch	2864.11816	0.31705	1	0
R-Branch	2905.40918	0.84236	0	1
R-Branch	2925.03515	0.89374	1	2
R-Branch	2943.89648	0.916	2	3
R-Branch	2962.24804	0.90156	3	4
R-Branch	2980.08984	0.84005	4	5
R-Branch	2997.16699	0.74405	5	6
R-Branch	3013.47949	0.46666	6	7

Model Fits

DBr

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* State Variables for DBr *

State Variable	Value	Units
Spring Constant (k)	384.0000	N·m ⁻¹
Mass 1	79.9040	amu
Mass 2	2.0141	amu
Reduced Mass (μ)	1.9646	amu

* Zero-Order-Model for DBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	1842.5381	1843.3052	(1842.9217±0.2712)	cm ⁻¹
Fundamental Frequency:	55.2379	55.2609	(55.2494±0.0081)	THz
Equilibrium Radius:	1.8849	2.2178	(2.0513±0.1177)	Å
Moment of Inertia:	6.9797	9.6628	(8.3213±0.9486)	amu·Å ²
Rotational Constant:	2.4152	1.7446	(2.0799±0.2371)	cm ⁻¹

* First-Order-Model for DBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	1839.1761	1839.1767	(1839.1764±0.0002)	cm ⁻¹
Fundamental Frequency:	55.1371	55.1371	(55.1371±0.0000)	THz
Equilibrium Radius:	1.4231	1.4112	(1.4171±0.0042)	Å
Moment of Inertia:	3.9785	3.9124	(3.9454±0.0234)	amu·Å ²
Rotational Constant:	4.2372	4.3088	(4.2730±0.0253)	cm ⁻¹
RoVib Coup. Constant:	0.0742	0.0911	(0.0826±0.0060)	cm ⁻¹

* Second-Order-Model for DBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	1839.0768	1839.6647	(1839.3708±0.2079)	cm ⁻¹
Fundamental Frequency:	55.1341	55.1518	(55.1429±0.0062)	THz
Equilibrium Radius:	1.4285	1.4449	(1.4367±0.0058)	Å
Moment of Inertia:	4.0089	4.1014	(4.0551±0.0327)	amu·Å ²
Rotational Constant:	4.2050	4.1103	(4.1576±0.0335)	cm ⁻¹
RoVib Coupling Constant:	0.0827	0.0481	(0.0654±0.0122)	cm ⁻¹
Centrifugal Dist. Const.:	-0.0004	0.0007	(0.0001±0.0004)	cm ⁻¹

DCI

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* State Variables for DC1 *

State Variable	Value	Units
Spring Constant (k)	480.0000	N·m ⁻¹
Mass 1	35.4530	amu
Mass 2	2.0141	amu
Reduced Mass (μ)	1.9058	amu

* Zero-Order-Model for DC1 *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2093.1347	2095.9062	(2094.5205±0.9799)	cm ⁻¹
Fundamental Frequency:	62.7506	62.8337	(62.7921±0.0294)	THz
Equilibrium Radius:	1.7201	2.0113	(1.8657±0.1030)	Å
Moment of Inertia:	5.6386	7.7098	(6.6742±0.7323)	amu·Å ²
Rotational Constant:	2.9897	2.1865	(2.5881±0.2839)	cm ⁻¹

* First-Order-Model for DC1 *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2090.4855	2090.2895	(2090.3875±0.0693)	cm ⁻¹
Fundamental Frequency:	62.6712	62.6653	(62.6682±0.0021)	THz
Equilibrium Radius:	1.2837	1.2695	(1.2766±0.0050)	Å
Moment of Inertia:	3.1404	3.0716	(3.1060±0.0243)	amu·Å ²
Rotational Constant:	5.3680	5.4882	(5.4281±0.0425)	cm ⁻¹
RoVib Coup. Constant:	0.1019	0.1239	(0.1129±0.0078)	cm ⁻¹

* Second-Order-Model for DC1 *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2090.3557	2090.3684	(2090.3621±0.0045)	cm ⁻¹
Fundamental Frequency:	62.6673	62.6677	(62.6675±0.0001)	THz
Equilibrium Radius:	1.2901	1.2733	(1.2817±0.0060)	Å
Moment of Inertia:	3.1721	3.0897	(3.1309±0.0291)	amu·Å ²
Rotational Constant:	5.3144	5.4560	(5.3852±0.0501)	cm ⁻¹
RoVib Coupling Constant:	0.1197	0.1170	(0.1183±0.0010)	cm ⁻¹
Centrifugal Dist. Const.:	-0.0012	0.0001	(-0.0005±0.0005)	cm ⁻¹

HBr

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@ HBr @
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* State Variables for HBr *

State Variable	Value	Units
Spring Constant (k)	382.0000	N·m ⁻¹
Mass 1	79.9040	amu
Mass 2	1.0078	amu
Reduced Mass (μ)	0.9953	amu

* Zero-Order-Model for HBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2562.5918	2563.3564	(2562.9741±0.2703)	cm ⁻¹
Fundamental Frequency:	76.8246	76.8475	(76.8360±0.0081)	THz
Equilibrium Radius:	1.8950	2.2186	(2.0568±0.1144)	Å
Moment of Inertia:	3.5742	4.8992	(4.2367±0.4685)	amu·Å ²
Rotational Constant:	4.7165	3.4409	(4.0787±0.4510)	cm ⁻¹

* First-Order-Model for HBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2558.1526	2557.7490	(2557.9508±0.1427)	cm ⁻¹
Fundamental Frequency:	76.6915	76.6794	(76.6854±0.0043)	THz
Equilibrium Radius:	1.4265	1.4084	(1.4175±0.0064)	Å
Moment of Inertia:	2.0254	1.9743	(1.9998±0.0181)	amu·Å ²
Rotational Constant:	8.3232	8.5386	(8.4309±0.0762)	cm ⁻¹
RoVib Coup. Constant:	0.2018	0.2549	(0.2283±0.0188)	cm ⁻¹

* Second-Order-Model for HBr *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2557.7660	2557.7490	(2557.7575±0.0060)	cm ⁻¹
Fundamental Frequency:	76.6799	76.6794	(76.6796±0.0002)	THz
Equilibrium Radius:	1.4414	1.4084	(1.4249±0.0117)	Å
Moment of Inertia:	2.0680	1.9743	(2.0211±0.0331)	amu·Å ²
Rotational Constant:	8.1517	8.5386	(8.3452±0.1368)	cm ⁻¹
RoVib Coupling Constant:	0.2626	0.2549	(0.2587±0.0027)	cm ⁻¹
Centrifugal Dist. Const.:	-0.0045	-0.0000	(-0.0023±0.0016)	cm ⁻¹

HCl

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@ HCl @
0000000

* State Variables for HCl *

State Variable	Value	Units
Spring Constant (k)	478.0000	N·m ⁻¹
Mass 1	35.4530	amu
Mass 2	1.0078	amu
Reduced Mass (μ)	0.9800	amu

* Zero-Order-Model for HCl *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2888.3684	2888.9510	(2888.6597±0.2060)	cm ⁻¹
Fundamental Frequency:	86.5911	86.6086	(86.5998±0.0062)	THz
Equilibrium Radius:	1.7350	1.9539	(1.8444±0.0774)	Å
Moment of Inertia:	2.9500	3.7412	(3.3456±0.2797)	amu·Å ²
Rotational Constant:	5.7144	4.5060	(5.1102±0.4272)	cm ⁻¹

* First-Order-Model for HCl *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2885.0550	2885.1642	(2885.1096±0.0386)	cm ⁻¹
Fundamental Frequency:	86.4918	86.4950	(86.4934±0.0012)	THz
Equilibrium Radius:	1.2908	1.2745	(1.2827±0.0058)	Å
Moment of Inertia:	1.6328	1.5919	(1.6123±0.0145)	amu·Å ²
Rotational Constant:	10.3243	10.5898	(10.4570±0.0939)	cm ⁻¹
RoVib Coup. Constant:	0.2761	0.3156	(0.2958±0.0139)	cm ⁻¹

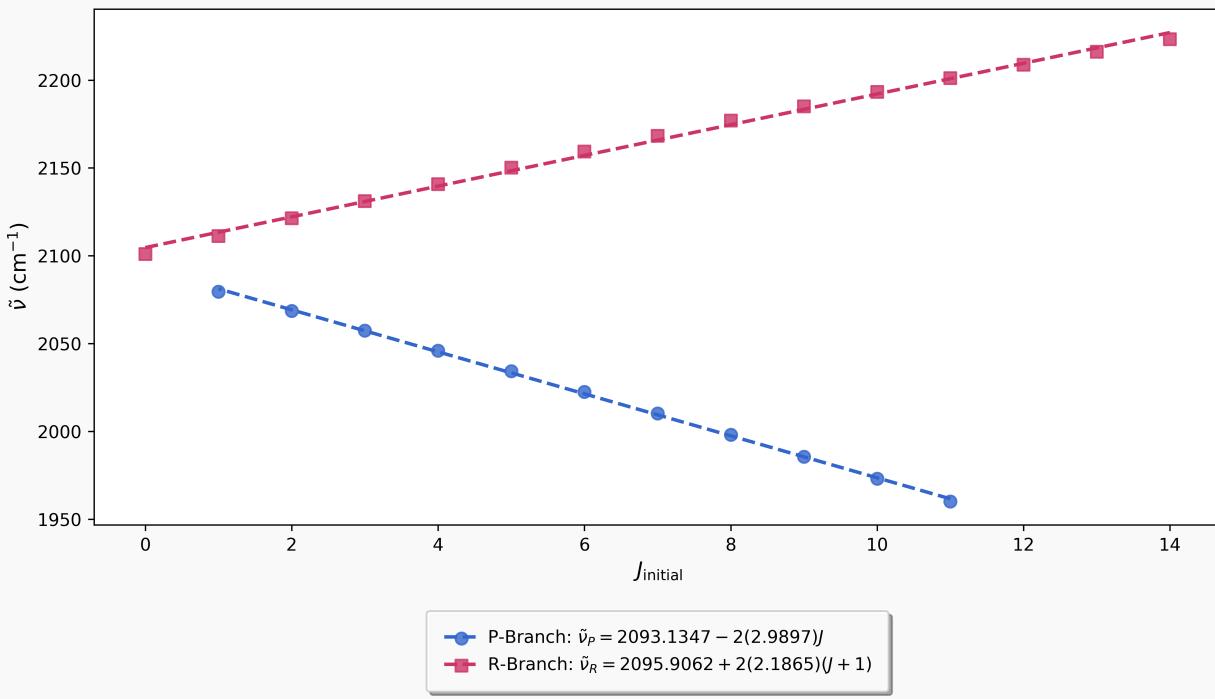
* Second-Order-Model for HCl *

Constant	P-Branch	R-Branch	Average	Units
Fundamental Wavenumber:	2885.0544	2885.4026	(2885.2285±0.1231)	cm ⁻¹
Fundamental Frequency:	86.4918	86.5022	(86.4970±0.0037)	THz
Equilibrium Radius:	1.2908	1.2865	(1.2887±0.0015)	Å
Moment of Inertia:	1.6329	1.6221	(1.6275±0.0038)	amu·Å ²
Rotational Constant:	10.3238	10.3927	(10.3583±0.0244)	cm ⁻¹
RoVib Coupling Constant:	0.2764	0.2495	(0.2629±0.0095)	cm ⁻¹
Centrifugal Dist. Const.:	-0.0000	0.0024	(0.0012±0.0008)	cm ⁻¹

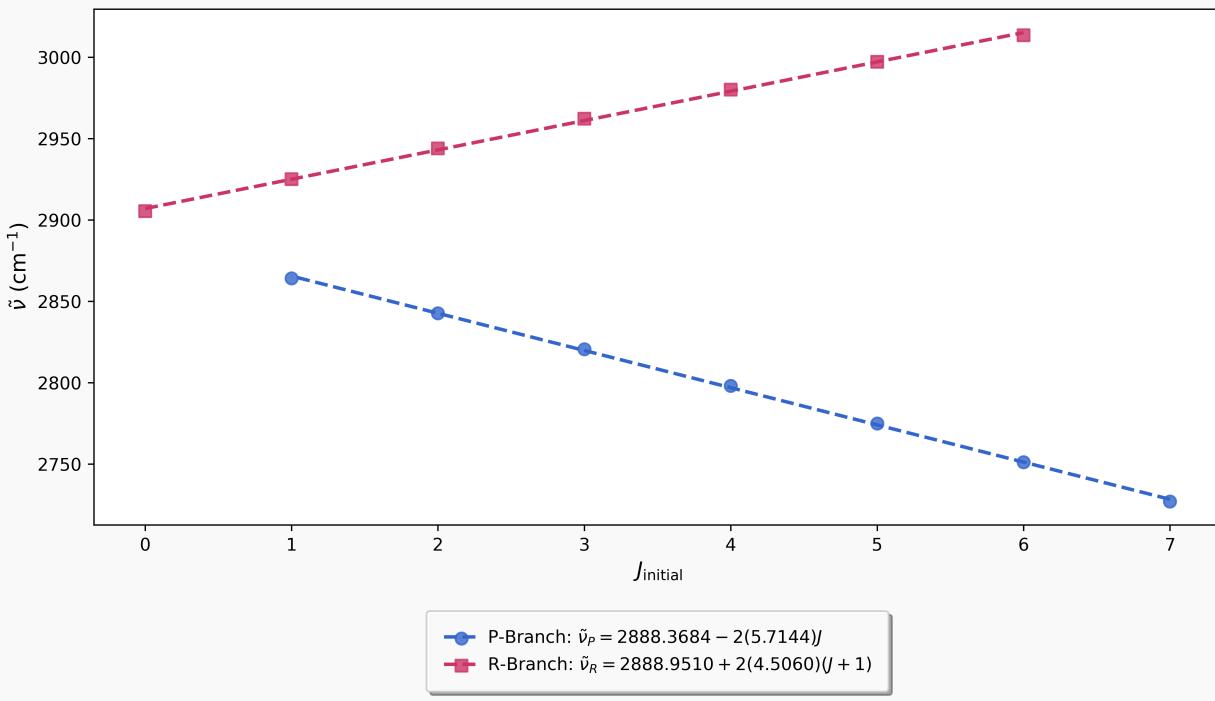
Zero Order Model



Zero-Order Model for DCI



Zero-Order Model for HCl



Background

The energy for the zero model approximation is given by:

$$E_0 = hf_0 \left(n + \frac{1}{2} \right) + hcBJ(J+1)$$

The zero order approximation assumes the diatomic molecule consists of two distinct systems: a simple harmonic oscillator (SHO) representing the vibrational energy, and a rigid rotator (RR) representing the rotational energy. The peak in a rovib spectra is therefore the sum of the change in vibrational energy and the change in rotational energy. The vibrational transition is from $n = 0$ to $n = 1$ ($n \rightarrow n + 1$), where $n = 0$ is at the fundamental vibrational frequency f_0 . The energy from this transition is given by

$$\begin{aligned}\Delta E_n &= E_n(n+1) - E_n(n) \\ &= hf_0 \left(n + 1 + \frac{1}{2} \right) - hf_0 \left(n + \frac{1}{2} \right) \\ &= hf_0 \left[\left(n + \frac{3}{2} \right) - \left(n + \frac{1}{2} \right) \right] \\ &= hf_0\end{aligned}$$

By the selection rules for rotational transitions, $\Delta J = \pm 1$, leading to the two observed branches corresponding to $J \rightarrow J - 1$ (the 'P-Branch') and $J \rightarrow J + 1$ (the 'R-Branch').

P-Branch Derivations

The change in energy for the P-Branch is given by

$$\begin{aligned}\Delta E_{J,P} &= E_J(J-1) - E_J(J) \\ &= hcB(J-1)(J-1+1) - hcB(J(J+1)) \\ &= hcB[J(J-1) - J(J+1)] \\ &= hcB(-2J) \\ &= -hc(2BJ)\end{aligned}$$

And the total change in energy for a given transition

$$\Delta E_{0,P} = \Delta E_n + \Delta E_{J,P}$$

$$\Delta E_{0,P} = hf_0 - hc(2BJ)$$

$$\frac{\Delta E_{0,P}}{hc} = \frac{f_0}{c} - 2BJ$$

$$\tilde{\nu}_P = \tilde{\nu}_0 - 2BJ$$

R-Branch Derivations

A similar approach can be used for the R-Branch to find the energy of a specific transition

$$\begin{aligned}
\Delta E_{J,R} &= E_J(J+1) - E_J(J) \\
&= hcB(J+1)(J+1+1) - hcB(J(J+1)) \\
&= hcB[(J+1)(J+2) - J(J+1)] \\
&= hcB(2J+2) \\
&= hc(2B)(J+1)
\end{aligned}$$

And now solving for the energy of the peak

$$\begin{aligned}
\Delta E_{0,R} &= \Delta E_n + \Delta E_J(J)_R \\
\Delta E_{0,R} &= hf_0 + hc(2B)(J+1) \\
\frac{\Delta E_{0,R}}{hc} &= \frac{f_0}{c} + 2B(J+1) \\
\tilde{\nu}_R &= \tilde{\nu}_0 + 2B(J+1)
\end{aligned}$$

Fundamental Wavenumber

The zero order fit assumes the $\tilde{\nu} = \tilde{\nu}_0 + 2B(J+1)$ and for the P-branch we get $\tilde{\nu} = \tilde{\nu}_0 - 2BJ$. After we perform a linear regression on the data for DBr, we get $\tilde{\nu}_R = 1843.3052 + 2(1.7446)(J+1)$ and $\tilde{\nu}_P = 1842.5381 - 2(2.4152)J$. The average value is therefore

$$\begin{aligned}
\tilde{\nu}_0 &= \frac{\tilde{\nu}_R + \tilde{\nu}_P}{2} \\
&= \frac{1842.5381 + 1843.3052}{2} \\
&\approx 1842.9217\text{cm}^{-1} \\
SD &= \sqrt{\frac{(1842.5381 - 1842.9217)^2 + (1843.3052 - 1842.9217)^2}{2}} \\
&\approx 0.383550\text{cm}^{-1} \\
SE &= \frac{SD}{\sqrt{2}} \\
&= \frac{0.383550}{\sqrt{2}} \\
&\approx 0.2712\text{cm}^{-1} \\
\tilde{\nu}_0 &= (1842.9 \pm 0.2712)\text{cm}^{-1}
\end{aligned}$$

Rotational Constant

B represents the rotational constant, which is inversely proportional to the molecule's moment of inertia, mass, and equilibrium radius. It is directly related to the spacing of successive peaks and is therefore proportional to the change in energy between transitions. Using DBr as the model, the derivation of B is shown below.

$$\begin{aligned}
 B &= \frac{B_R + B_P}{2} \\
 &= \frac{1.7446 + 2.4152}{2} \\
 &= 2.0799\text{cm}^{-1} \\
 SD &= \sqrt{\frac{(1.7446 - 2.0799)^2 + (2.4152 - 2.0799)^2}{2}} \\
 &= 0.3353\text{cm}^{-1} \\
 SE &= \frac{SD}{\sqrt{2}} \\
 &= \frac{0.3353}{\sqrt{2}} \\
 &\approx 0.2371\text{cm}^{-1} \\
 \mathbf{B} &= (\mathbf{2.0799 \pm 0.2371}) \text{ cm}^{-1}
 \end{aligned}$$

Equilibrium Radius

The equation for the rotational constant is $B = \frac{h}{8\pi^2 c I}$ where $I = \mu r_e^2$. Rearranging gives $r_e = \sqrt{\frac{h}{8\pi^2 c \mu B}}$. For the R-Branch, the calculated r_e is

$$\begin{aligned}
 r_{e,R} &= \sqrt{\frac{h}{8\pi^2 c \mu_{\text{DBr}} B_R}} \\
 &= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (1.7446 \times 10^{-8} \text{\AA}^{-1})}} \\
 &\approx 2.2178 \text{\AA}
 \end{aligned}$$

For the P-Branch, r_e is

$$\begin{aligned}
 r_{e,P} &= \sqrt{\frac{h}{8\pi^2 c \mu_{DBr} B_P}} \\
 &= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (2.4152 \times 10^{-8} \text{\AA}^{-1})}} \\
 &\approx 1.8849 \text{\AA}
 \end{aligned}$$

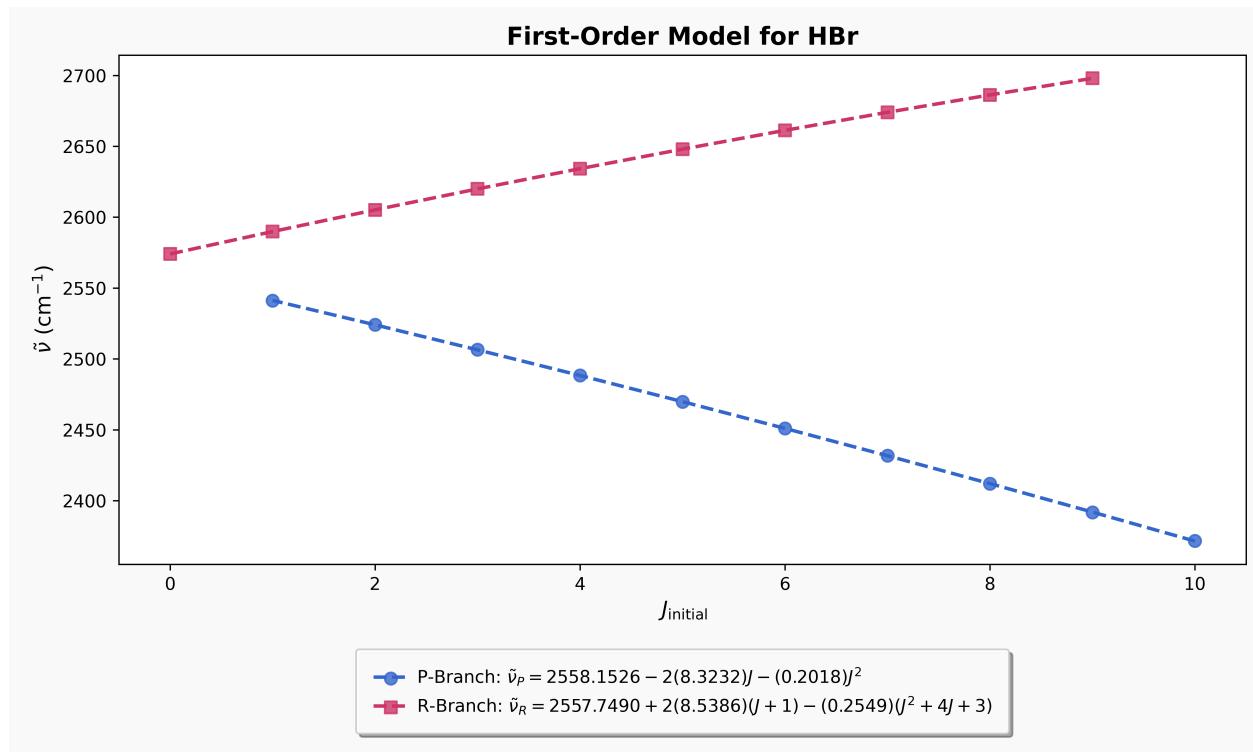
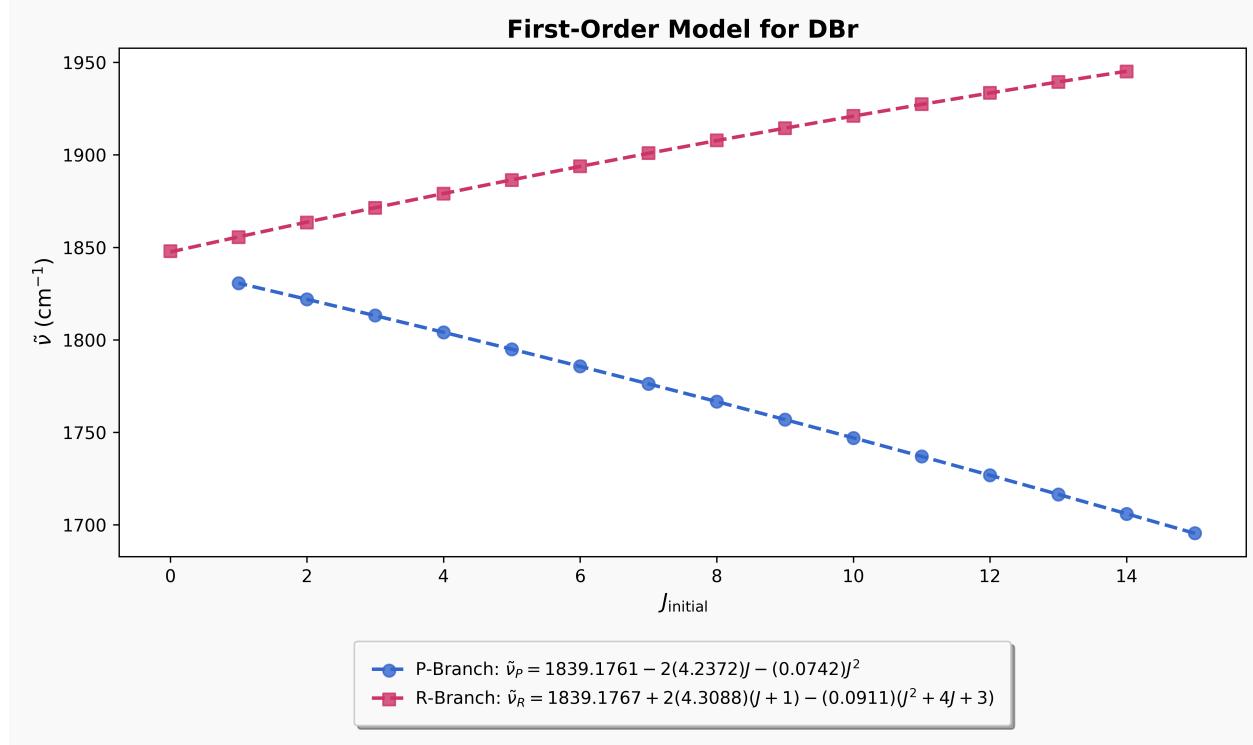
The average value is therefore

$$\begin{aligned}
 r_e &= \frac{r_{e,R} + r_{e,P}}{2} \\
 &= \frac{2.2178 + 1.8849}{2} \\
 &\approx 2.05135 \text{\AA} \\
 SD &= \sqrt{\frac{(2.2178 - 2.05135)^2 + (1.8849 - 2.05135)^2}{2}} \\
 &\approx 0.16645 \text{\AA} \\
 SE &= \frac{SD}{\sqrt{2}} \\
 &= \frac{0.16645}{\sqrt{2}} \\
 &\approx 0.1177 \text{\AA} \\
 \mathbf{r}_e &= (2.0513 \pm 0.1177) \text{\AA}
 \end{aligned}$$

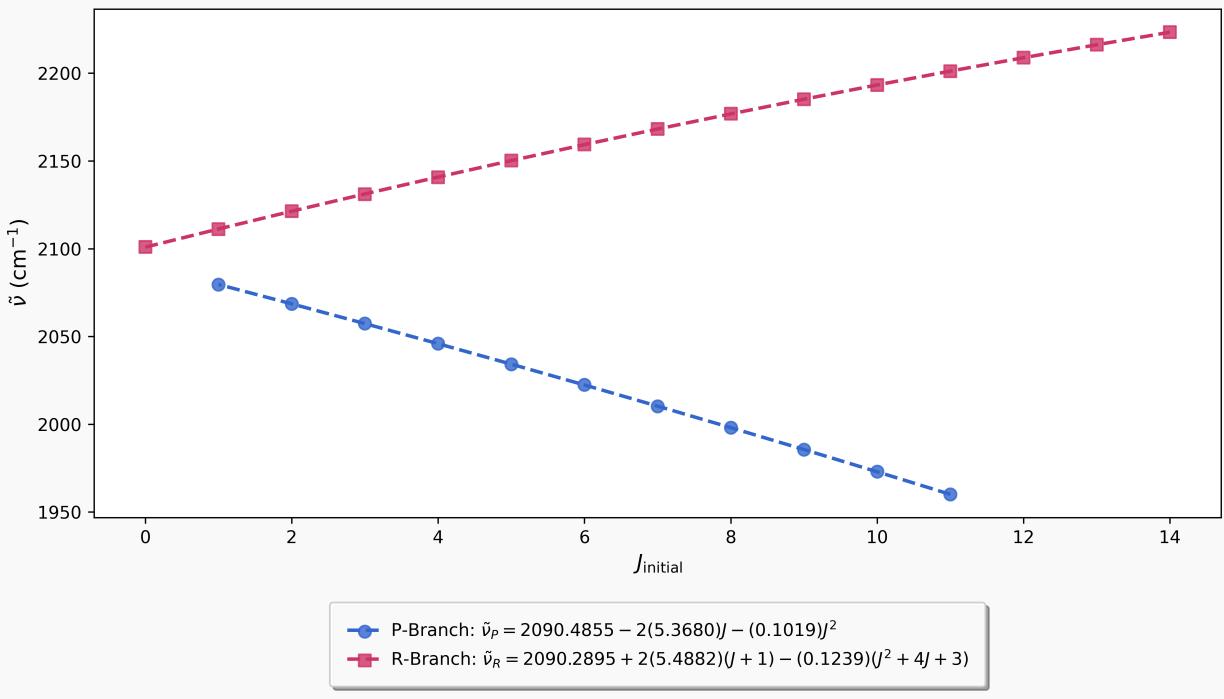
Moment of Inertia

The moment of inertia for the P-branch is $I_P \approx 6.9797 \text{amu} \cdot \text{\AA}^2$ and for the R-Branch $I_R \approx 9.6628 \text{amu} \cdot \text{\AA}^2$. This gives an average of $(8.3213 \pm 0.9486) \text{amu} \cdot \text{\AA}^2$

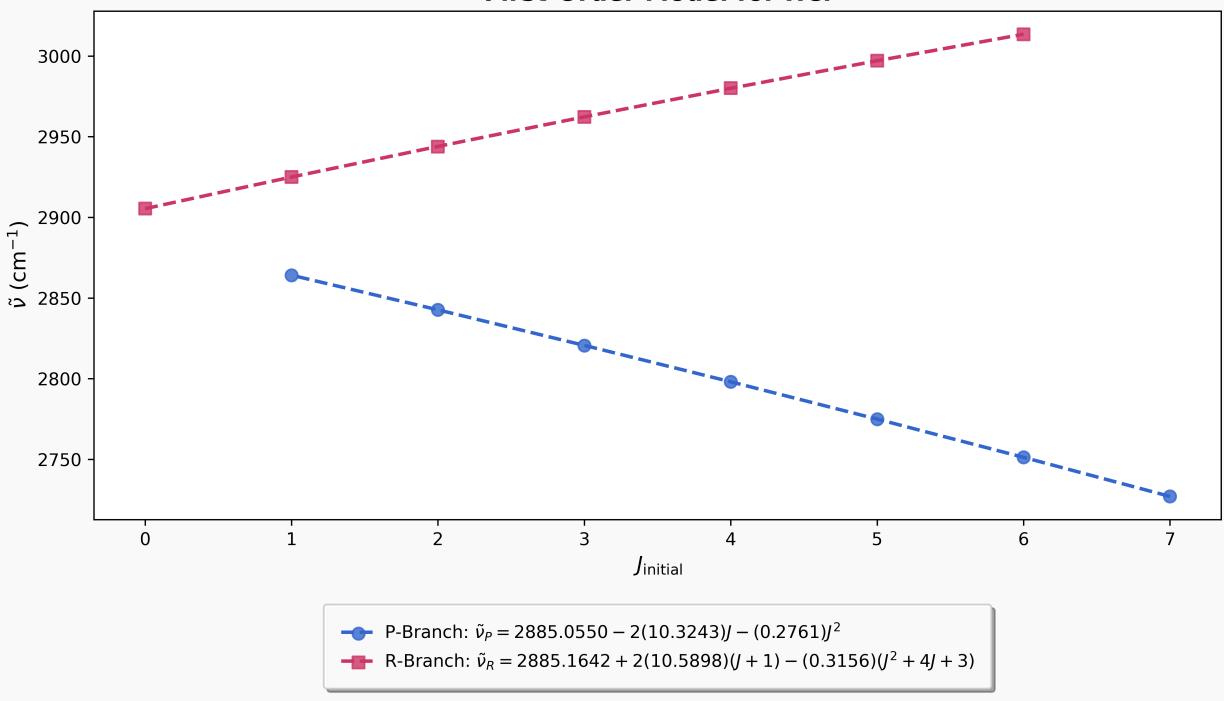
First Order Model



First-Order Model for DCI



First-Order Model for HCl



Background

The equation for the first order model is

$$E_1 = hf_0 \left(n + \frac{1}{2} \right) + hcBJ(J+1) - hca \left(n + \frac{1}{2} \right) J(J+1)$$

Like the zero order model, the first order approximation assumes the diatomic molecule consists of two systems: a simple harmonic oscillator (SHO) representing the vibrational energy, and a rigid rotator (RR) representing the rotational energy. In reality the two systems are not isolated systems, since the bond length and angular frequency are coupled to both vibration and rotation. The first order model therefore introduces a second term, α , which accounts for this. Since the rotational constant, B , is inversely proportional to the bond length, α will adjust the value of the rotational constant by accounting for larger non-ideal bond lengths. The magnitude of α is affected by the vibrational quantum number, n , since at higher vibrational energies the bond length will increase, and similarly the vibrational quantum number, J . The rotational energy of the molecule contributes a small proportion of the total energy w.r.t. the contribution from vibrational energy. Therefore, α will be small when compared to B . The peak in a rovib spectra is thus the difference between sum of the change in vibrational energy and the change in rotational energy, and the coupling factor.

P-Branch Derivations

The first order energies for the P-Branch are given by

$$\begin{aligned} \Delta E_{\alpha,P} &= E(n+1, J-1)_\alpha - E(n, J)_\alpha \\ &= hca \left(n + 1 + \frac{1}{2} \right) (J-1)(J-1+1) - hca \left(n + \frac{1}{2} \right) (J(J+1)) \\ &= hca \left[\left(n + \frac{3}{2} \right) (J^2 - J) - \left(n + \frac{1}{2} \right) (J^2 + J) \right] \\ &= hca \left[J^2 n + \frac{3J^2}{2} - Jn - \frac{3J}{2} - J^2 n - Jn - \frac{J^2}{2} \right] \\ &= hcaJ(J-2(n+1)) \end{aligned}$$

With the position of the peaks given by

$$\begin{aligned} \Delta E_{1,P} &= \Delta E_n + \Delta E_{J,P} - \Delta E_{\alpha,P} \\ \Delta E_{1,P} &= hf_0 - hc(2BJ) - hcaJ(J-2(n+1)) \\ \frac{\Delta E_{1,P}}{hc} &= \frac{f_0}{c} - J[2B + \alpha(J-2(n+1))] \\ \tilde{\nu}_P &= \tilde{\nu}_0 - J[2B + \alpha(J-2(n+1))] \\ \text{Sub } n = 0: \quad \tilde{\nu}_P &= \tilde{\nu}_0 - 2BJ - \alpha J^2 \end{aligned}$$

R-Branch Derivations

The first order energies for the R-branch are given by

$$\begin{aligned}
\Delta E_{\alpha,R} &= E(n+1, J+1)_\alpha - E(n, J)_\alpha \\
&= hc\alpha \left(n + 1 + \frac{1}{2} \right) (J+1)(J+1+1) - hc\alpha \left(n + \frac{1}{2} \right) (J(J+1)) \\
&= hc\alpha \left[\left(n + \frac{3}{2} \right) (J^2 + 3J + 2) - \left(n + \frac{1}{2} \right) (J^2 + J) \right] \\
&= hc\alpha [J^2 + 4J + 2Jn + 2n + 3] \\
&= hc\alpha [J(J+4) + 2n(J+1) + 3]
\end{aligned}$$

With the position of the peaks given by

$$\begin{aligned}
\Delta E_{1,R} &= \Delta E_n + \Delta E_{J,R} - \Delta E_{\alpha,R} \\
\Delta E_{1,R} &= hf_0 + hc(2B)(J+1) - hc\alpha [J(J+4) + 2n(J+1) + 3] \\
\frac{\Delta E_{1,R}}{hc} &= \frac{f_0}{c} + 2B(J+1) - \alpha [J(J+4) + 2n(J+1) + 3] \\
\tilde{\nu}_R &= \tilde{\nu}_0 + 2B(J+1) - \alpha [J(J+4) + 2n(J+1) + 3] \\
\text{Sub } n = 0: \quad \tilde{\nu}_R &= \tilde{\nu}_0 + 2B(J+1) - \alpha (J^2 + 4J + 3)
\end{aligned}$$

Fundamental Wavenumber

The first order fit describes the peak positions of the R-Branch with $\tilde{\nu} = \tilde{\nu}_0 + 2B(J+1) - \alpha (J^2 + 4J + 3)$ and for the P-branch we get $\tilde{\nu} = \tilde{\nu}_0 - 2BJ$. After we perform a linear regression on the data for DBr, we get $\tilde{\nu}_R = 1839.1767 + 2(4.3088)(J+1) - (0.0911)(J^2 + 4J + 3)$, and $\tilde{\nu}_P = 1839.1761 - 2(4.2372)J - (0.0742)^2$. Calculating the average gives

$$\begin{aligned}
\tilde{\nu}_0 &= \frac{\tilde{\nu}_R + \tilde{\nu}_P}{2} = \frac{1839.1767 + 1839.1761}{2} \approx 1839.1764 \text{ cm}^{-1} \\
SD &= \sqrt{\frac{(1839.1767 - 1839.1764)^2 + (1839.1761 - 1839.1764)^2}{2}} \approx 0.0003 \text{ cm}^{-1} \\
SE &= \frac{SD}{\sqrt{2}} = \frac{0.0003}{\sqrt{2}} \approx 0.0002 \text{ cm}^{-1} \\
\tilde{\nu}_0 &= (1842.9 \pm 0.0002) \text{ cm}^{-1}
\end{aligned}$$

Rotational Constant

$$\begin{aligned}B &= \frac{B_R + B_P}{2} \\&= \frac{4.3088 + 4.2372}{2} \\&\approx 4.2730\text{cm}^{-1}\end{aligned}$$

$$\begin{aligned}SD &= \sqrt{\frac{(4.3088 - 4.2730)^2 + (4.2372 - 4.2730)^2}{2}} \\&\approx 0.0358\text{cm}^{-1}\end{aligned}$$

$$\begin{aligned}SE &= \frac{SD}{\sqrt{2}} \\&= \frac{0.0358}{\sqrt{2}} \\&\approx 0.0253\text{cm}^{-1}\end{aligned}$$

$$\mathbf{B = (4.2730 \pm 0.0253) cm^{-1}}$$

Rotational-Vibrational Coupling Constant

$$\begin{aligned}\alpha &= \frac{\alpha_R + \alpha_P}{2} \\&= \frac{0.0911 + 0.0742}{2} \\&= 0.0826\text{cm}^{-1}\end{aligned}$$
$$\begin{aligned}SD &= \sqrt{\frac{(0.0911 - 0.0826)^2 + (0.0742 - 0.0826)^2}{2}} \\&= 0.00845015\text{cm}^{-1}\end{aligned}$$

$$\begin{aligned}SE &= \frac{SD}{\sqrt{2}} \\&= \frac{0.00845015}{\sqrt{2}} \\&\approx 0.006\text{cm}^{-1}\end{aligned}$$

$$\alpha = (0.0826 \pm 0.006) \text{ cm}^{-1}$$

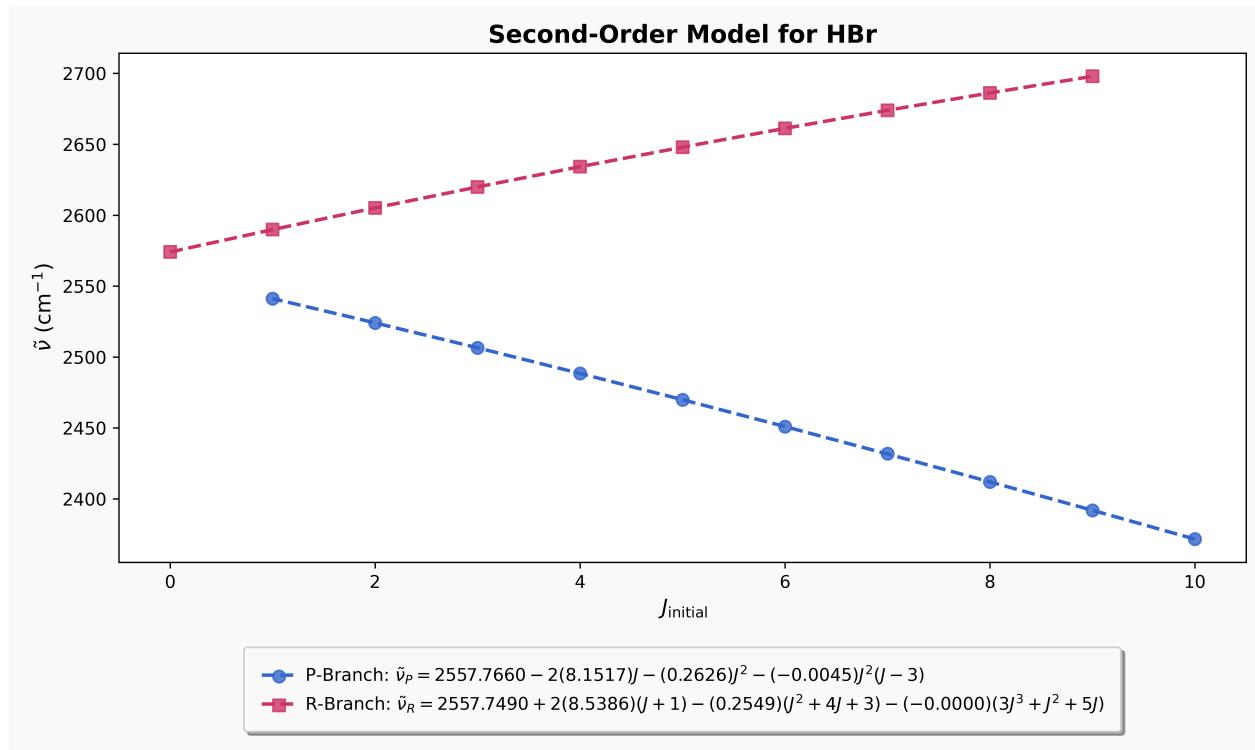
Equilibrium Radius

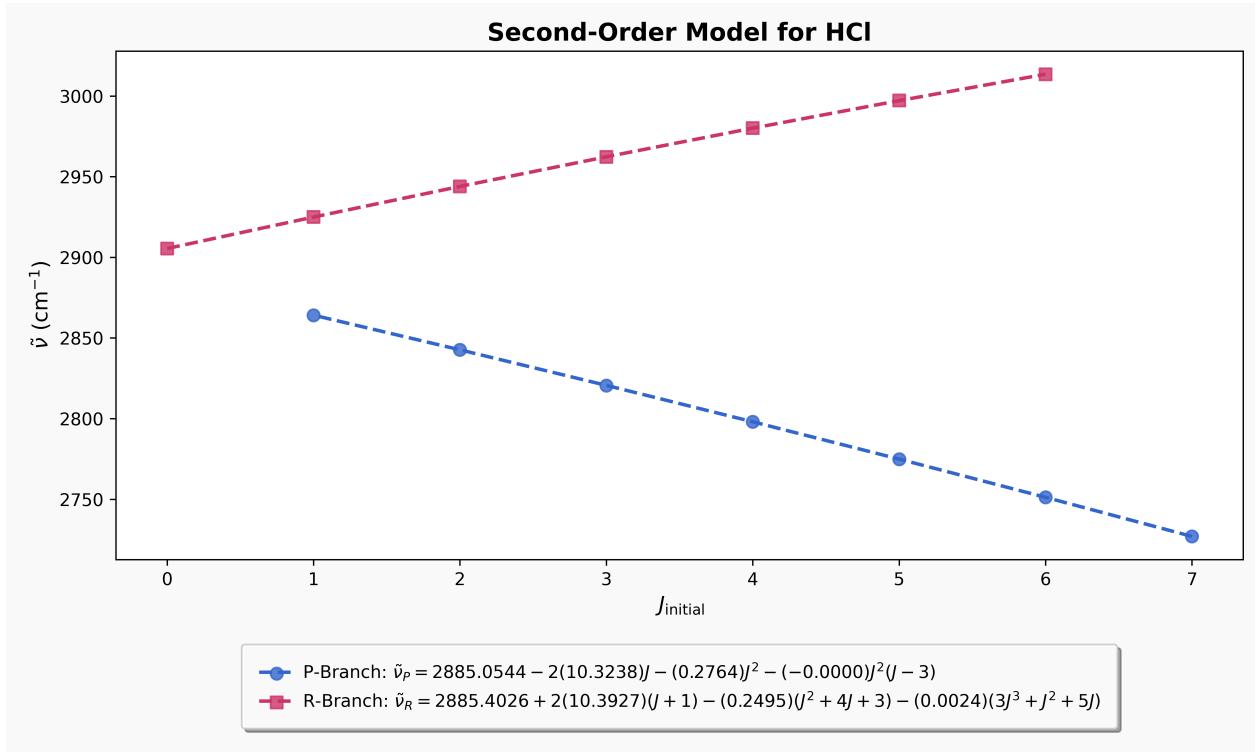
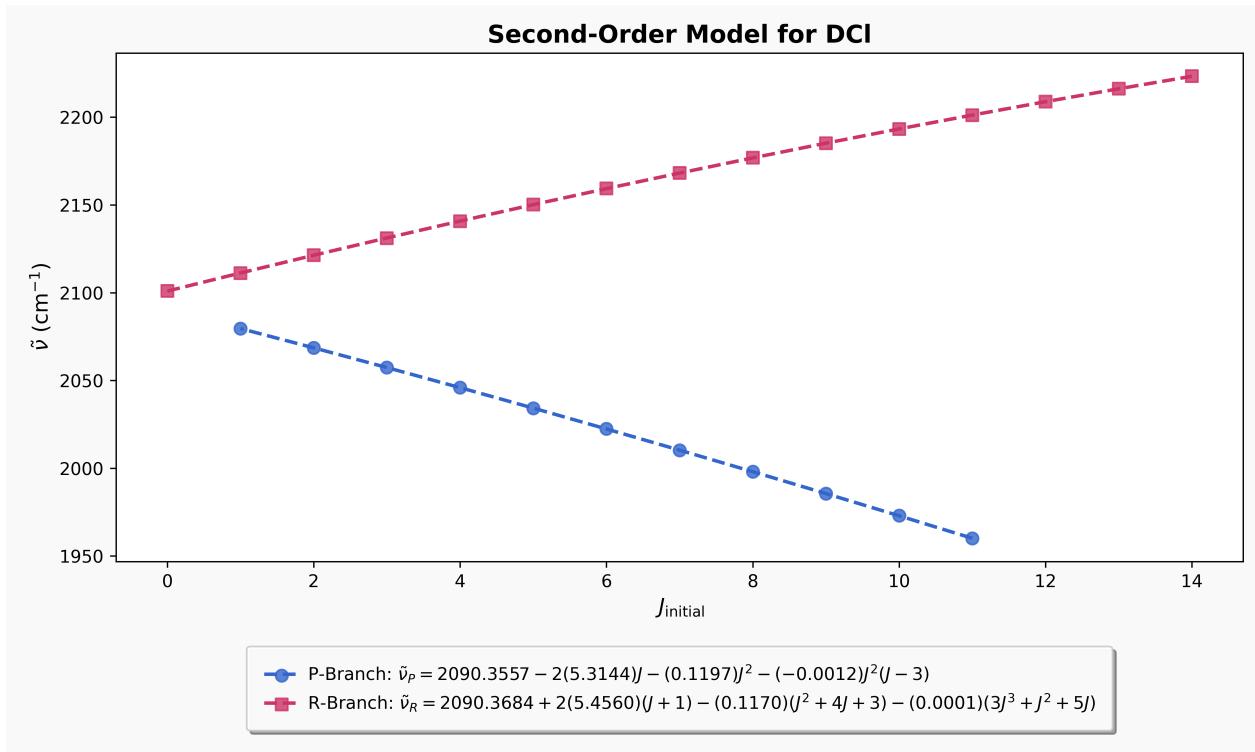
$$\begin{aligned}
r_{e,R} &= \sqrt{\frac{h}{8\pi^2 c \mu_{DBr} B_R}} \\
&= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (4.3088 \times 10^{-8} \text{\AA}^{-1})}} \\
&\approx 1.411 \text{\AA} \\
r_{e,P} &= \sqrt{\frac{h}{8\pi^2 c \mu_{DBr} B_P}} \\
&= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (4.2372 \times 10^{-8} \text{\AA}^{-1})}} \\
&\approx 1.423 \text{\AA} \\
r_e &= \frac{r_{e,R} + r_{e,P}}{2} \\
&= \frac{1.411 + 1.423}{2} \\
&\approx 1.417 \text{\AA} \\
SD &= \sqrt{\frac{(1.411 - 1.417)^2 + (1.423 - 1.417)^2}{2}} \\
&\approx 0.006 \text{\AA} \\
SE &= \frac{SD}{\sqrt{2}} \\
&= \frac{0.006}{\sqrt{2}} \\
&\approx 0.0042 \text{\AA} \\
\mathbf{r}_e &= (1.417 \pm 0.0042) \text{\AA}
\end{aligned}$$

Moment of Inertia

The moment of inertia for the P-branch is $I_P \approx 3.9785 \text{amu} \cdot \text{\AA}^2$ and for the R-Branch $I_R \approx 3.9124 \text{amu} \cdot \text{\AA}^2$. This gives an average of $(3.9454 \pm 0.0234) \text{amu} \cdot \text{\AA}^2$

Second Order Model





Background

The second order approximation is:

$$E_2 = hf_0 \left(n + \frac{1}{2} \right) + hcBJ(J+1) - hc\alpha \left(n + \frac{1}{2} \right) J(J+1) - hc\delta J^2 (J+1)$$

The second order approximation assumes the diatomic molecule consists of two coupled systems: a simple harmonic oscillator (SHO) representing the vibrational energy, and a rigid rotator (RR) representing the rotational energy. In contrast with the first order approximation, it takes into account the effects of centrifugal distortion caused by the rotation of the molecule. The centrifugal force of the rotation of the molecule causes the bond length, r_e , to increase. Since the rotational constant, B , is inversely proportional to the bond length, the centrifugal distortion term, δ , corrects for this by lowering the overall calculated energy. Since this term only concerns centrifugal distortion, it is only based w.r.t. the rotational quantum number, J . Since rotational energy contributes a relatively small amount to the overall energy of the system, this corrective factor will be very small. The peak in a rovib spectra is therefore the difference between sum of the change in vibrational energy and the change in rotational energy, and the sum of the coupling and centrifugal distortion terms.

P-Branch Derivations

The second order energies for the P-Branch are given by

$$\begin{aligned} \Delta E_{\delta,P} &= hc\delta (J-1)^2 (J-1+1) - hc\delta J^2 (J+1) \\ &= hc\delta [(J-1)(J-1)(J) - J^3 - J] \\ &= hc\delta [J^3 - 3J^2] \\ &= hc\delta J^2 (J-3) \end{aligned}$$

With the position of the peaks given by

$$\begin{aligned} \Delta E_{2,P} &= \Delta E_n + \Delta E_{J,P} - \Delta E_{\alpha,P} - \Delta E_{\delta,P} \\ \Delta E_{2,P} &= hf_0 - hc(2BJ) - hc\alpha J(J-2(n+1)) - hc\delta J^2 (J-3) \\ \frac{\Delta E_{2,P}}{hc} &= \frac{f_0}{c} - 2BJ - \alpha J^2 - \delta J^2 (J-3) \\ \tilde{\nu}_P &= \tilde{\nu}_0 - 2BJ - J^2 [\alpha + \delta (J-3)] \end{aligned}$$

R-Branch Derivations

The second order energies for the R-branch are given by

$$\begin{aligned}\Delta E_{\delta,R} &= hc\delta \left[(J+1)^2 (J+1+1) - J^2 (J+1) \right] \\ &= hc\delta [3J^3 + J^2 + 5J]\end{aligned}$$

With the position of the peaks given by

$$\begin{aligned}\Delta E_{2,R} &= \Delta E_n + \Delta E_{J,R} - \Delta E_{\alpha,R} - \Delta E_{\delta,R} \\ \frac{\Delta E_{2,R}}{hc} &= \tilde{\nu}_0 + 2B(J+1) - \alpha[J(J+4)+3] - hc\delta[3J^3 + J^2 + 5J]\end{aligned}$$

Fundamental Wavenumber

After we perform a linear regression on the data for DBr, we get for the R-Branch $\tilde{\nu}_R = 1839.6647 + 2(4.1103)(J+1) - (0.0481)(J^2 + 4J + 3) - (0.0007)(3J^3 + J^2 + 5J)$, and for the P-branch $\tilde{\nu}_P = 1839.0768 - 2(4.2050)J - (0.0827)J^2 + (0.0004)J^2(J-3)$. Calculating the average gives

$$\begin{aligned}\tilde{\nu}_0 &= \frac{\tilde{\nu}_R + \tilde{\nu}_P}{2} = \frac{1839.6647 + 1839.0768}{2} \approx 1839.3708\text{cm}^{-1} \\ SD &= \sqrt{\frac{(1839.6647 - 1839.3708)^2 + (1839.0768 - 1839.3708)^2}{2}} \\ &\approx 0.293950\text{cm}^{-1} \\ SE &= \frac{SD}{\sqrt{2}} \\ &= \frac{0.293950}{\sqrt{2}} \approx 0.2079\text{cm}^{-1} \\ \tilde{\nu}_0 &= (1839.3708 \pm 0.2079)\text{cm}^{-1}\end{aligned}$$

Rotational Constant

$$B = \frac{B_R + B_P}{2} = \frac{4.1103 + 4.2050}{2} \approx 4.1576\text{cm}^{-1}$$

$$SD = \sqrt{\frac{(4.2050 - 4.1576)^2 + (4.1103 - 4.1576)^2}{2}} \approx 0.0473500\text{cm}^{-1}$$

$$SE = \frac{SD}{\sqrt{2}} = \frac{0.0473500}{\sqrt{2}} \approx 0.0335\text{cm}^{-1}$$

$$\mathbf{B} = (4.1576 \pm 0.0335) \text{ cm}^{-1}$$

Rotational-Vibrational Coupling Constant

$$\alpha = \frac{\alpha_R + \alpha_P}{2} = \frac{0.0481 + 0.0827}{2} \approx 0.0654\text{cm}^{-1}$$

$$SD = \sqrt{\frac{(0.0481 - 0.0654)^2 + (0.0827 - 0.0654)^2}{2}} \approx 0.0173\text{cm}^{-1}$$

$$SE = \frac{SD}{\sqrt{2}} = \frac{0.0173}{\sqrt{2}} \approx 0.0122\text{cm}^{-1}$$

$$\alpha = (0.0654 \pm 0.0122) \text{ cm}^{-1}$$

Centrifugal Distortion Constant

$$\delta = \frac{\delta_R + \delta_P}{2} = \frac{0.0007 - 0.0004}{2} \approx 0.00015\text{cm}^{-1}$$

$$SD = \sqrt{\frac{(0.0007 - 0.00015)^2 + (-0.0004 - 0.00015)^2}{2}} \approx 0.00055\text{cm}^{-1}$$

$$SE = \frac{SD}{\sqrt{2}} = \frac{0.00055}{\sqrt{2}} \approx 0.00039\text{cm}^{-1}$$

$$\delta = (0.00015 \pm 0.00039) \text{ cm}^{-1}$$

Equilibrium Radius

$$\begin{aligned}
r_{e,R} &= \sqrt{\frac{h}{8\pi^2 c \mu_{\text{DBr}} B_R}} \\
&= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (4.1103 \times 10^{-8} \text{\AA}^{-1})}} \\
&\approx 1.449 \text{\AA} \\
r_{e,P} &= \sqrt{\frac{h}{8\pi^2 c \mu_{\text{DBr}} B_P}} \\
&= \sqrt{\frac{0.0399031221 \text{\AA}^2 \cdot \text{amu/fs}}{(8\pi^2) (2.99792458 \times 10^3 \text{\AA/fs}) (1.9646 \cdot \text{amu}) (4.2050 \times 10^{-8} \text{\AA}^{-1})}} \\
&\approx 1.4285 \text{\AA} \\
r_e &= \frac{r_{e,R} + r_{e,P}}{2} \\
&= \frac{1.449 + 1.4285}{2} \\
&\approx 1.4367 \text{\AA} \\
SD &= \sqrt{\frac{(1.449 - 1.4367)^2 + (1.4285 - 1.4367)^2}{2}} \\
&\approx 0.0104530 \text{\AA} \\
SE &= \frac{SD}{\sqrt{2}} \\
&= \frac{0.0104530}{\sqrt{2}} \\
&\approx 0.0074 \text{\AA} \\
\mathbf{r}_e &= (1.4367 \pm 0.0074) \text{\AA}
\end{aligned}$$

Moment of Inertia

The moment of inertia for the P-branch is $I_P \approx 4.0089 \text{amu} \cdot \text{\AA}^2$ and for the R-Branch $I_R \approx 4.1014 \text{amu} \cdot \text{\AA}^2$. This gives an average of $(4.0551 \pm 0.0327) \text{amu} \cdot \text{\AA}^2$