Workshop: Rovibrational and rovibronic spectra of gaseous HCl

Quantum aspects of physical chemistry

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This workshop illustrates that rovibrational and rovibronic spectra of diatomic molecules are a rich source of information about their structure in their different electronic states. With experience, you will be able to tell with just a glance at a molecular spectrum quite a lot about the internal details of the molecule.

■ Rovibrational transition energies

The contribution to the energy of a diatomic molecule in the rigid rotor and harmonic oscillator approximations is

$$\frac{E_{i,J}}{h\,c} = \tilde{\nu}_e (i - 1/2) + \tilde{B}_e\, J(J+1).$$

For ${}^{1}\text{H}\,{}^{35}\text{Cl}$ in its electronic ground state, the harmonic oscillator angular frequency is $\tilde{\nu}_e = 2990.9476\ \text{cm}^{-1}$ and twice the rigid rotor rotational constant is $2\,\tilde{B}_e = 21.1874\ \text{cm}^{-1}$. In this case, then, the vibrational energy contribution is about 100 times the rotational contribution. More generally, values of $\tilde{\nu}_e$ are typically at least an order of magnitude larger that typical values of $\tilde{B}_e$.

A consequence of this large difference in contributions to the total energy is that the change in vibrational quantum number determines whether a rovibrational transition is an absorption or an emission. If $i \to i+1$, the transition is an absorption and if $i \to i-1$, the transition is an emission—independently of the change in rotational quantum number. For each kind of vibrational transition, the rotational quantum number can increase or decrease, that is, vibrational excitation is accompanied by both increases and decreases in rotational quantum numbers.

The part of the spectrum corresponding to an increase in rotational quantum number is known as the *R branch*, and the part of the spectrum corresponding to a decrease in rotational quantum number is known as the *P branch.*

> 1. Show that the expressions for the energies of the *P* and *R* branch transitions for the vibrational absorption $i \to i+1$ are

$$\tilde{\nu}_P(i \to i+1) = \frac{\Delta E_P(i \to i+1)}{h\,c} = \tilde{\nu}_e - 2\,\tilde{B}_e\, J,$$

$$\tilde{\nu}_R(i \to i+1) = \frac{\Delta E_R(i \to i+1)}{h\,c} = \tilde{\nu}_e + 2\,\tilde{B}_e (J+1).$$

> 2. Show that the expressions for the energies of the P and R branch transitions for the vibrational emission $i \to i-1$ are

$$\tilde{\nu}_P(i \to i-1) = -\frac{\Delta E_P(i \to i-1)}{h\,c} = \tilde{\nu}_e + 2\,\tilde{B}_e\,J,$$

$$\tilde{\nu}_R(i \to i-1) = -\frac{\Delta E_R(i \to i-1)}{h\,c} = \tilde{\nu}_e - 2\,\tilde{B}_e(J+1).$$

■ Thermal population of rotational levels

Molecules in a gas can be in one of a range of rotational states. The higher the temperature, the greater the range of possible J values. For a large sample of molecules in thermal equilibrium the population of rotational energy values is given by the Boltzmann distribution, according to which the fraction of molecules with rotational quantum number J is

$$f(J) = (2\,J+1)\,e^{-B_e\,J(J+1)/(k_\mathrm{B}\,T)}\,/\,Z.$$

In this expression $k_\mathrm{B} = 1.38065 \times 10^{-23}$ J/K is the Boltzmann constant, T is the temperature in K, and the constant Z is defined as

$$Z = \sum_{J=0}^{\infty} (2\,J+1)\,e^{-B_e\,J(J+1)/(k_\mathrm{B}\,T)},$$

so that the sum of all of the fractions $f(J)$ is one.

> 3. Show that this definition of Z insures that $\sum_{J=0}^{\infty} f(J) = 1$.

Evaluating the constant *Z*

To compute numerical values of the fractions $f(J)$ we first need to determine the numerical value of Z. There are two ways to do this.

The first way to evaluate Z, is to evaluate its defining ecpression to within a specified accuracy. We do this by carrying out the sum in the definition of Z explicitly, including as many terms as are necessary for the sum to no longer change. The number of terms needed will increase as the temperature is increased.

The second way is to evaluate Z approximately by assuming that J varies continuously, rather than in integer steps. With this assumption the expression for Z becomes an integral,

$$Z \approx \int_0^{\infty} (2\,J+1)\,e^{-B_e\,J(J+1)/(k_\mathrm{B}\,T)}\,dJ.$$

We can next change the integration variable to $x = J(J+1)$. Since $dx/dJ = 2\,J+1$, we can evaluate the integral approximation to be

$$Z \approx \int_0^{\infty} e^{-B_e\,x/(k_\mathrm{B}\,T)}\,dx = k_\mathrm{B}\,T\,/\,B_e.$$

This approximation scheme will be the more accurate the more the variation in J is effectively continuous. This will be the case when $B_e\,/\,(k_\mathrm{B}\,T) \ll 1$, that is, when $T \gg B_e\,/\,k_\mathrm{B}$, since then the

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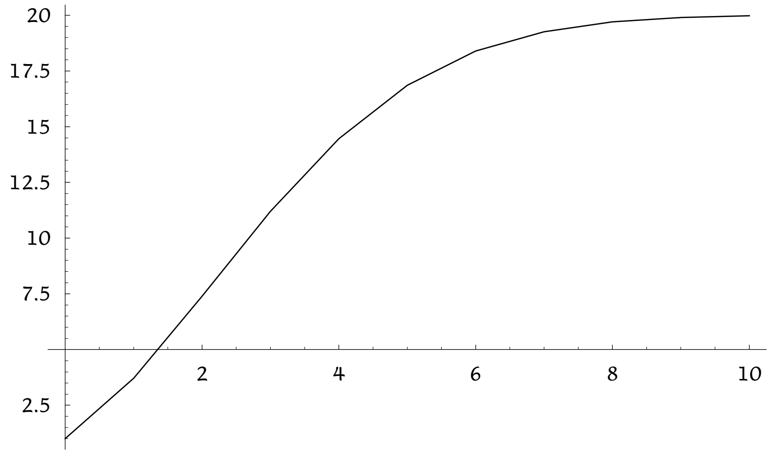
exponent in the integrand will change negligibly when J changes by one integer. For $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$, $B_e / k_\mathrm{B} = 15.242$ K. This means that for $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ at typical laboratory temperatures and above, the integral approximation should be reasonable.

Here is a comparison of the exact results (obtained, as described, above by adding successive terms to the sum until its value stops changing) and the approximate results.



T (K)	Z exact	Z approx	% error
10	1.14284	0.656084	42.5918
80	5.59519	5.24867	6.19317
100	6.90464	6.56084	4.97928
300	20.0193	19.6825	1.68215
1000	65.9427	65.6084	0.507035
10000	656.417	656.084	0.0507786

Exact and approximate normalization factor Z of gaseous $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ rotational levels at different temperatures.

The comparison shows that at room temperature, the accuracy is better than 2%.

> 4. Verify the approximate value of Z given in the table for 300 K.

Evaluating the fractional populations $f(J)$

For a given temperature, once the corresponding value of Z is determined, we can evaluate the fractions $f(J)$. Let's work with the temperature 300 K and use the corresponding exact value $Z = 20.0193$. With these values specified, we can evaluate the fractional population of each rotational level, $f(J)$.

We need to determine the fractions of all of the rotational levels that contribute appreciably to the population. A way to determine how many values of J to include is to see how many values of J are necessary for the total of all fractions to equal one, to some specified precision. As example, here is a plot of

$$\sum_{J=0}^{J_\mathrm{max}} f(J) = \sum_{J=0}^{J_\mathrm{max}} (2\,J + 1)\, e^{-B_e\, J(J+1)/(k_\mathrm{B}\, T)} / Z$$

for $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ at 300 K for different value of J_max.

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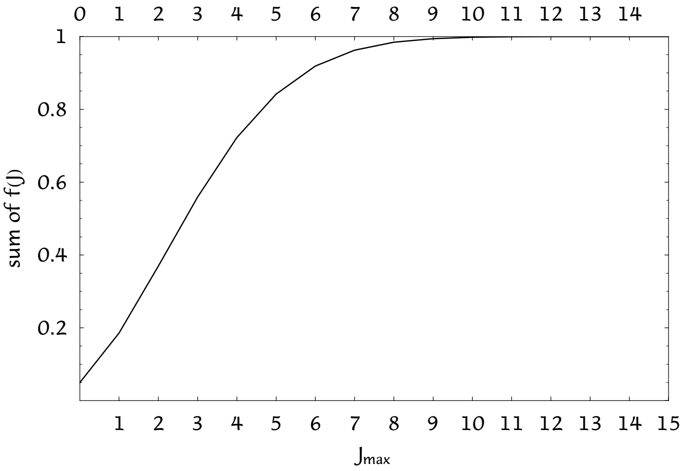

Cumulative total of fractional populations of gaseous ^{1}H^{35}Cl rotational levels at 300 K versus J_{max}.

The plot shows that if we include J values up to 10, we will account for all of the significantly populated rotational levels of ^{1}H^{35}Cl at 300 K. Here are the populations, expressed as percentages, of the individual levels.

J	f(J) as %
0	4.995
1	13.54
2	18.41
3	19.01
4	16.27
5	11.97
6	7.687
7	4.355
8	2.189
9	0.9805
10	0.3923

Percentage populations of gaseous ^{1}H^{35}Cl rotational levels at 300 K.

■ Rovibrational absorption spectrum

With the vibrational absorption transition energies,

$$\tilde{\nu}_P(i \to i+1) = \frac{\Delta E_P(i \to i+1)}{h\,c} = \tilde{\nu}_e - 2\,\tilde{B}_e\,J,$$

$$\tilde{\nu}_R(i \to i+1) = \frac{\Delta E_R(i \to i+1)}{h\,c} = \tilde{\nu}_e + 2\,\tilde{B}_e(J+1),$$

and fractional rotational level populations,

$$f(J) = (2\,J+1)\,e^{-B_e\,J(J+1)/(k_{\text{B}}\,T)}\,/\,Z,$$

we can construct the ^{1}H^{35}Cl *rovibrational* absorption spectrum. We'll do this by indicating each rovibrational transition by a vertical line at the corresponding energy, and making the height of the line equal to the fractional population of the initial J value of the transition.

For ^{1}H^{35}Cl in its electronic ground state, the harmonic oscillator level separation is $\tilde{\nu}_e = 2990.9476$ cm^{-1} and twice the rigid rotor rotational constant is $2\,\tilde{B}_e = 21.1874$ cm^{-1}. Using these values, we can write the energies of vibrational absorption P and R branches as, in cm^{-1},

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$$\tilde{\nu}_P = \frac{\Delta E_P(i \to i+1)}{h\,c} = 2990.9476 - 21.1874\,J$$

$$\tilde{\nu}_R = \frac{\Delta E_R(i \to i+1)}{h\,c} = 2990.9476 + 21.1874\,(J+1)$$

Setting the zero of energy at the energy of the pure vibrational transition, $\tilde{\nu}_e = 2990.9476\ \text{cm}^{-1}$, we can construct the following table of the energies and relative intensities of the *P* branch.

energy (cm^{-1})	intensity (%)
−21.1874	13.5376
−42.3748	18.4133
−63.5622	19.0051
−84.7496	16.274
−105.937	11.9673
−127.124	7.68715
−148.312	4.35515
−169.499	2.18938
−190.687	0.980519
−211.874	0.392303

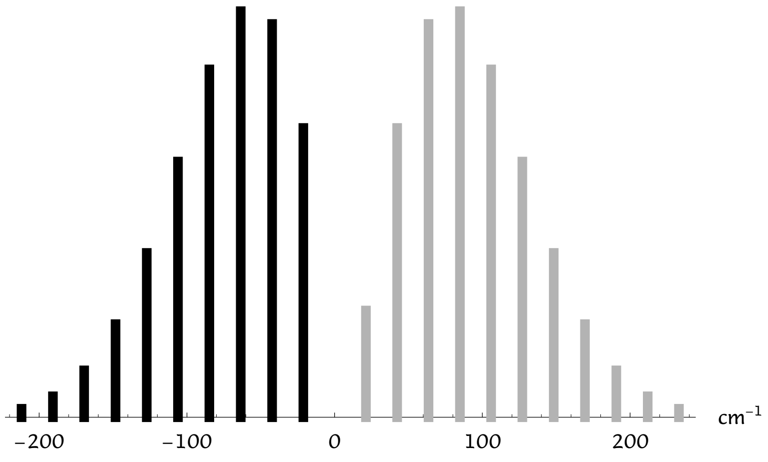
Energies and percentage populations for ${}^{1}\text{H}\,{}^{35}\text{Cl}$ rovibrational *P* branch at 300 K.

Here is the corresponding table of the energies and relative intensities of the *R* branch.

energy (cm^{-1})	intensity (%)
21.1874	4.99519
42.3748	13.5376
63.5622	18.4133
84.7496	19.0051
105.937	16.274
127.124	11.9673
148.312	7.68715
169.499	4.35515
190.687	2.18938
211.874	0.980519
233.061	0.392303

Energies and percentage populations for ${}^{1}\text{H}\,{}^{35}\text{Cl}$ rovibrational *R* branch at 300 K.

Finally, here is a representation of the spectrum.



Rovibrational spectrum of ${}^{1}\text{H}\,{}^{35}\text{Cl}$ at 300 K.The zero of energy is the energy of the pure vibrational transition, $\tilde{\nu}_e = 2990.9476\ \text{cm}^{-1}$.

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> 5. How would the spectrum change if the temperature were increased by a factor of ten?

> 6. How would the spectrum change for a molecule with rotational constant ten times smaller?

> 7. How would the spectrum change if instead of pure $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$, naturally occurring HCl gas were used?

> 8. Use the exact value for Z given earlier for 10 K to repeat the calculations of the fractional populations $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ at 10 K to verify the numerical values shown below, and so verify that including only three values of J at 10 K accounts for all of the populated levels, to four significant figures.

J	f(J) as %
0	87.5
1	12.45
2	0.0467

Fractional populations of gaseous $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ rotational levels at 10 K.

■ Determining gas temperature from rotational bands

Because the distribution of rotational levels depends on temperature, we can use the details of rotational lines in the spectrum to determine temperature. An approximate approach is to again assume that J varies continuously. Then we can predict which rotational line of the R branch that has the greatest intensity by finding the value of J for which the fractional population reaches a maximum. The maximum will be the value of J for which $d\, f(J)/d J = 0$. The result is

$$J_{\text{peak}} = \sqrt{\frac{k_{\mathrm{B}}\,T}{2\,B_e}} - \frac{1}{2}.$$

> 9. Show that for $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ 300 K, $J_{\text{peak}} = 2.6 \approx 3$.

> 10. Does this value of J match the value of J at the peak of the R branch of the 300 K spectrum shown above?

Here is a spectrum of $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ taken at an unknown temperature. What is the value of the temperature?

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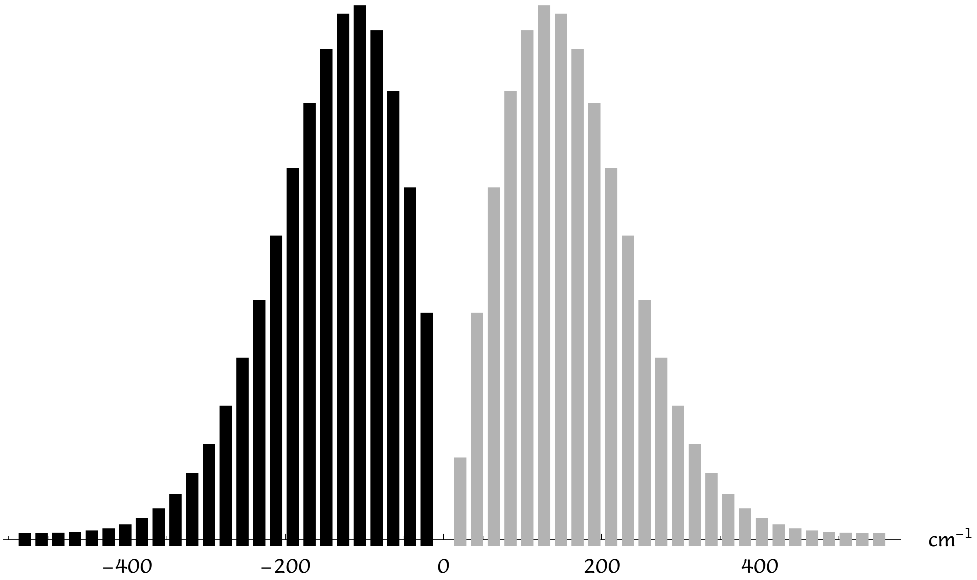

Rovibrational spectrum of ^{1}H^{35}Cl at an unknown temperature. The zero of energy is the energy of the pure vibrational transition, $\tilde{\nu}_e = 2990.9476$ cm^{-1}.

> 11. Use the spectrum to estimate the value of the temperature?

■ Rovibronic transition energies

A *rovibronic* transition is one in which there is a change in electronic state accompanied by a change in both vibrational and rotational states. Let's consider the case of electronic excitation, in which the final electronic state has more energy than the initial electronic state.

The expression for the internal energy of the initial rovibronic state, j, is its rovibrational energy plus the electronic energy at the equilibrium internuclear distance,

$$\frac{E_{i,J}}{h\,c} = \frac{E_j(R_e)}{h\,c} + \tilde{\nu}_{e,j}(i_j - 1/2) + \tilde{B}_{e,j}\, J_j(J_j + 1).$$

The electronic state index j is added as a subscript on the vibrational quantum number i and the rotational quantum number J so we can distinguish between the vibrational and rotational quantum numbers of the two electronic states participating in the transition. The electronic state index j is also added as a subscript on the constants ω and B_e. This is necessary since the nuclei experience different potential energy curves, $E_j(R)$, for different electronic states, and as a result the harmonic frequency and rigid rotor rotational constants will be different in different electronic states.

As example, let's take for the initial sate, $j = i$, ^{1}H^{35}Cl in its electronic ground state. The equilibrium internuclear distance is 1.27455 Å, the harmonic oscillator frequency is $\tilde{\nu}_{e,i} = 2990.9476$ cm^{-1}, and twice the rigid rotor rotational constant is $2\,\tilde{B}_{e,i} = 21.1874$ cm^{-1}. Let's take as final state, $j = f$, the excited electronic state of ^{1}H^{35}Cl that is 77293 cm^{-1} above the ground state,

$$\tilde{\nu}_0 = \frac{E_{j_f}(R_{e,j_f}) - E_{j_i}(R_{e,j_i})}{h\,c} = 77293\,\text{cm}^{-1}.$$

For the excited state the equilibrium internuclear distance is 2.512 Å, the harmonic oscillator frequency is $\tilde{\nu}_{e,f} = 877.16$ cm^{-1}, and twice the rigid rotor rotational constant is $2\,\tilde{B}_{e,f} = 5.454$ cm^{-1}.

> 12. Account qualitatively for the differences in $\tilde{\nu}_e$ and $\tilde{B}_e$ and for the excited electronic state compared to the values for the ground state. *Hint*: Compare the values for R_e.

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With this information we have what we need to investigate the spectrum of rovibronic transitions between these states. The general expression for possible rovibronic excitation energies is

$$\tilde{\nu} = \tilde{\nu}_0 + \tilde{\nu}_f\left(i_f - \frac{1}{2}\right) - \tilde{\nu}_i\left(i_i - \frac{1}{2}\right) + \tilde{B}_{e,f}\, J_f(J_f + 1) - \tilde{B}_{e,i}\, J_i(J_i + 1).$$

in a somewhat simplified notation where subscripts i and f indicate initial and final electronic state.

Since the vibrational wave functions of the two electronic states pertain to different electronic potential energies, the restriction that vibrational quantum number may change only by a single unit no longer holds. Rather, any vibrational quantum number change is possible. The restriction that rotational quantum number may change by a single unit still does hold, however, since the rotational wave functions do not depend on the electronic potential energies.

To get a feeling for the spectrum, let's look at the part of the spectrum in which the molecule is in its vibrational ground state in both electronic states; that is, let's assume that $i_i = i_f = 1$.

> 13. Show that in this case the possible transition energies are

$$\tilde{\nu} = \tilde{\nu}_0 + \frac{1}{2}\,(\tilde{\nu}_f - \tilde{\nu}_i) + \tilde{B}_{e,f}\, J_f(J_f + 1) - \tilde{B}_{e,i}\, J_i(J_i + 1).$$

The electronic and vibrational contributions set energy of the "center" of spectrum, $\tilde{\nu}_{\mathrm{c}} = \tilde{\nu}_0 + (\tilde{\nu}_f - \tilde{\nu}_i)/2$.

> 14. Show spectrum center is at $\tilde{\nu}_{\mathrm{c}} = 76236.11\,\mathrm{cm}^{-1}$.

As in the rovibrational case, we can get separate expressions for the rovibronic *P* and *R* branches.

> 15. Show that the energy of the *P* branch transition $J_i = J \to J_f = J - 1$ is

$$\tilde{\nu}_P = \tilde{\nu}_{\mathrm{c}} + \tilde{B}_{e,f}\, J(J - 1) - \tilde{B}_{e,i}\, J(J + 1).$$

Here are the energies $\tilde{\nu}_P - \tilde{\nu}_{\mathrm{c}}$ and populations for $^1\mathrm{H}\,^{35}\mathrm{Cl}$ *P* branch at 80 K.

J initial	energy (cm^{-1})	intensity (%)
1	−21.19	36.63
2	−42.11	28.49
3	−62.76	12.72
4	−83.15	3.561
5	−103.3	0.6475
6	−123.1	0.07778

Energies $\tilde{\nu}_P - \tilde{\nu}_{\mathrm{c}}$ and percentage populations for $^1\mathrm{H}\,^{35}\mathrm{Cl}$ rovibronic *P* branch at 80 K.

> 16. Verify the values for energy and intensity for the $J = 1$ member of the *P* branch.

> 17. Show that the energy of the *R* branch transition $J_i = J \to J_f = J + 1$ is

$$\tilde{\nu}_R = \tilde{\nu}_{\mathrm{c}} + \tilde{B}_{e,f}(J + 1)\,(J + 2) - \tilde{B}_{e,i}\, J(J + 1).$$

Here are the energies $\tilde{\nu}_R - \tilde{\nu}_0$ and populations for $^1\mathrm{H}\,^{35}\mathrm{Cl}$ *R* branch at 80 K.

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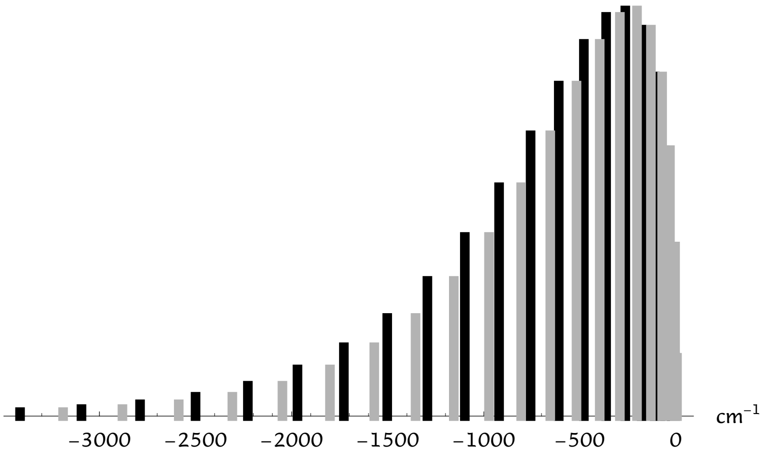
> 18. Verify the values for energy and intensity for the $J = 1$ member of the R branch.

J initial	energy (cm^{-1})	intensity (%)
0	5.454	17.87
1	−4.825	36.63
2	−30.84	28.49
3	−72.58	12.72
4	−130.1	3.561
5	−203.3	0.6475
6	−292.2	0.07778

Energies $\tilde{\nu}_R - \tilde{\nu}_c$ and percentage populations for $^1\text{H}^{35}\text{Cl}$ rovibronic R branch at 80 K.

Here is the rovibronic spectrum at 1000 K.



Rovibronic spectrum of $^1\text{H}^{35}\text{Cl}$ at 1000 K. The zero of energy is the energy of the pure electronic transition, $\tilde{\nu}_c$ = 76236.11 cm^{-1}.

This spectrum is very different from the rovibrational spectra we constructed earlier. It has what is known as a rotational *band head*: Absorption abruptly terminates at 5.454 cm^{-1} above $\tilde{\nu}_c$. This band head is seen at all temperatures.

> 19. Explain the origin of the band head.

> 20. Explain whether there could be a rovibronic transition that comes to a head at low energy rather than high energy?

> 21. Explain whether there could be a rovibronic transition that does not have a band head?

The extension of these ideas to polyatomic molecules leads to even more riches. But that is for another course!

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