Advanced Chemistry 2008

Vibration - Rotation Spectrum of a Diatomic Molecule

Analysis of the Fundamental Bands of the $H^{79}Br$ and $H^{81}Br$ Molecules

- The vibration-rotation spectrum of the HBr molecule in the gas phase was recorded with the FTIR spectrometer at 0.1 cm^{-1} resolution using a 10 cm gas cell as the sample cell.

- Two spectral features were noted and attributed to the two isotopes of HBr: H^{79}Br and H^{81}Br. For each of these species, P and R branches were observed. It was noted that in general the peaks corresponding to each isotope was about the same intensity.

For the following questions, you must write descriptive, clear answers using complete sentences. Show all work. When you are done, you will submit a packet of work which will include answers to these questions.

Indicate the question numbers clearly when reporting your answers. You can either type your answers or handwrite them (legibly please).

QUESTIONS:

1. Determine approximately the relative abundances of ^{79}Br and ^{81}Br isotopes based on the above information. How does this compare with the relative abundances of ^{35}Cl and ^{37}Cl?

2. Using the FTIR Software the following frequencies of the P and R peaks for the two isotopes H^{79}Br and H^{81}Br in cm^{-1} units were determined. Assign the ground state rotational quantum numbers (J") to each of the peaks.

HBr Isotope 1 Spectral Lines

R lines		P lines
2590.95 7		2542.25 3
2606.24 7		2525.09 9
2621.04 5		2507.49 5
2635.34 4		2489.44 9
2649.14 3		2470.97 6
2662.42 7		2452.08 1
2675.19 3		2432.76 5
2687.43 2		2413.05 1
2699.13 1		2392.94 5
2710.29 3		2372.45 1
2720.90 2		2351.58 2
2730.96 8		

HBr Isotope 2 Spectral Lines

R lines		P lines
2590.55 6		2541.87
2605.84 2		2524.71 7
2620.63 6		2507.11 8
		2489.08 7
2634.93		
2648.72 1		2470.61 7
2662.00 1		2451.73
2674.76 1		2432.43
2687.00 1		2412.72
2698.69 8		2392.61 2
2709.85 8		2372.13 3
2720.47 9		2351.26 2
2730.54 9		

3. Look up the rotational constant (B value) for HCl. Use this value to predict a reasonable B value (or at least a range) for HBr. Show all work.

4. Now it is time to fit your data. Recall that

$$T(v,J) = \omega_e\ (v+\tfrac{1}{2}) - \omega_e x_e\ (v+\tfrac{1}{2})^2 + B_e J\ (J + 1) - D_e\ J^2\ (J+1)^2 - \alpha_e\ (v+\tfrac{1}{2})\ J(J+1)$$

Note: D_e = centrifugal distortion constant

$$B_v = B_e - \alpha_e\ (v+\tfrac{1}{2}) \quad \text{and} \quad D_v = D_e - \beta_e\ (v+\tfrac{1}{2})$$

We will assume that β_e is negligibly small.

$$\therefore\ D_v = D_e \qquad\qquad B_e = h/8\,\pi^2\,I_e c \qquad\qquad I_e = \mu\,r_e^2$$

For the 1-0 band (fundamental band) of the absorption spectrum of HBr,

$$\Delta v = +1 \qquad \Delta J = \pm 1 \qquad\qquad \Delta J = +1 \Rightarrow \text{R branch}$$
$$\Delta J = -1 \Rightarrow \text{P branch}$$
$$v'' = 0 \quad v' = 1$$

Draw an energy level diagram to show the P and R branches of the fundamental band. Do this for only one isotope. Clearly label the vibrational and rotational quantum numbers with the correct symbol for each energy level.

5. Show that (please show all work) for the R branch (in cm^{-1})

$$\nu_R = (v' - v''\,)\omega_e - \omega_e x_e\ [(v' - v''\,)\ (v' + v'' + 1)] + (B_{v'} + B_{v''}\,)(J'' + 1) +$$
$$(B_{v'} - B_{v''}\,)(J'' + 1)^2 - 4D_e\ (J'' + 1)^3$$

and for the P branch (in cm^{-1})

$$\nu_P = (v' - v''\,)\omega_e - \omega_e x_e\ [(v' - v''\,)\ (v' + v'' + 1)] - (B_{v'} + B_{v''}\,)J'' + (B_{v'} - B_{v''}\,)J''^2 + 4D_e\ J''^3$$

6. Using $J'' = J$, show that: (please show all work)

- $$\frac{R\ (J) - P(J)}{4\ (J + 1/2)} = B_{v'} - 2D_e\ (J^2 + J + 1) \qquad\qquad\qquad \textbf{Equation A}$$

- $$\frac{R\ (J - 1) - P\ (J + 1)}{4\ (J + 1/2)} = B_{v''} - 2D_e\ (J^2 + J + 1) \qquad\qquad\qquad \textbf{Equation B}$$

- $$\frac{R\,(J)+P\,(J+1)}{2} = (v' - v'')\omega_e\,[1 - x_e(v' + v'' + 1)] + (B_{v'} - B_{v''})(J+1)^2 \qquad \textbf{Equation C}$$

Note that from Equations (A), (B), and (C) above:

- A graph of $\dfrac{R\,(J) - P(J)}{4\,(J + 1/2)}$ versus $(J^2 + J + 1)$ is a straight line with slope $= -2De$, and intercept $= B_{v'}$

- A graph of $\dfrac{R\,(J - 1) - P\,(J + 1)}{4\,(J + 1/2)}$ versus $(J^2 + J + 1)$ is a straight line with slope $= -2De$, and intercept $= B_{v''}$

- A graph of $\dfrac{R\,(J) + P\,(J + 1)}{2}$ versus $(J + 1)^2$ is a straight line with slope $= (B_{v'} - B_{v''})$ and intercept $= (v' - v'')\omega_e\,[1 - x_e(v' + v'' + 1)]$

It is important to note that:
$(v' - v'')\omega_e\,[1 - x_e(v' + v'' + 1)]$ is the **<u>band origin</u>** of the vibrational band. For the 1-0 fundamental band, the band origin is denoted by $v_0\,(1 \leftarrow 0)$

i.e. $v_0\,(1 \leftarrow 0)$ $=$ $(v' - v'')\omega_e\,[1 - x_e(v' + v'' + 1)]$ $=$ $\omega_e - 2\,\omega_e\,x_e$

7. Using MS Excel (please **do not** use any other software for this purpose), plot the three graphs given above for **each of the** HBr isotopes. Use the <u>regression analysis</u> tool of Excel to plot these graphs. Use the residual plots to verify that you have made correct rotational quantum number assignments (i.e. you have a "good fit"). If you did the analysis correctly, the B values you get for each HBr isotope should be close to the values you estimated using HCl data (in 4 above). If this is not so, you cannot proceed. Go back, check everything you did until you get B values you can live with!!

8. Once you have a good fit, print your Excel worksheets including input data for the graphs, regression analysis output, residual plots and line fit plots. Print the three graphs (for each isotope) on separate sheets so that you can expand them for clarity. Print the input data on a separate sheet and the regression output on a separate sheet. Label your worksheets and graphs so that the reader can easily identify the corresponding worksheets and graphs. When printing worksheets make sure that **<u>all</u>** the significant figures are visible in the input data and the regression output (you will have to set the column width to do this). All worksheets and graphs <u>must be</u> printed in the **<u>landscape mode</u>** (not portrait mode).

9. Now what is left to do is "polishing up" your work for presentation. Do the following steps. Once you have a complete analysis for both isotopes of HBr, obtain values for the following molecular parameters for each isotope. Show all work where calculations are needed.

B_e, B_0, B_1, α_e, D_e, $v_0(1\text{-}0)$ and r_e

After you complete these calculations, round off to the <u>correct number</u> of significant figures (you must keep 4 decimal points throughout your analysis and round off only just before reporting your work).

10. Please show values before you round off and after you round off. Generate a table (shown below) to report molecular parameters. Include correct units for each parameter. Modify this table if necessary. Add an appropriate title and use MS Word to generate the table. Use Greek letters, superscripts and subscripts where necessary.

Molecular Parameters	Before rounding off		After rounding off	
	$H^{79}Br$	$H^{81}Br$	$H^{79}Br$	$H^{81}Br$
$\nu_0(1\text{-}0)$				
B_0				
B_1				
B_e				
α_e				
D_e				
r_e				

11. Compare your values with <u>literature values</u>. Generate a table for comparing your results with literature values. Be sure to use the correct number of significant figures and include the correct units for each parameter. Add an appropriate title to the table. Are there any significant discrepancies? If so, give reasons for these discrepancies.

Molecular Parameters	This Experiment		Literature Values	
$\nu_0(1\text{-}0)$	$H^{79}Br$	$H^{81}Br$	$H^{79}Br$ [a]	$H^{81}Br$ [b]
B_0				
B_1				
B_e				
α_e				
D_e				
r_e				

[a] These values were obtained from reference 1 [reference 1 is given on line]

12. Tabulate the line positions for the two isotopes of HBr as shown below. Add as many rows as needed to the table to report your data. Be sure to round off to the correct number of significant figures. Include correct units. Add an appropriate title to the table.

Rotational Quantum Number (J")	$H^{79}Br$		$H^{81}Br$	
	P Branch	R Branch	P Branch	R Branch
0				
1				
2				
3				
4…etc				

13. If the band origin of the 2-0 band of $H^{79}Br$ is 5028.08 cm^{-1}, calculate the values of ω_e and $\omega_e x_e$ for the $H^{79}Br$ molecule. Show all work.

14. At what frequency would you expect to see the second overtone for $H^{79}Br$? At what frequency would you expect to see the 2-1 hot band for $H^{79}Br$? Draw an energy level diagram to show the fundamental band, first overtone, second overtone and the 2-1 hot band. Label these bands clearly in your diagram and label the vibrational levels with the correct quantum numbers.

15. What do you expect the intensities of these overtones and hot bands to be, relative to the fundamental band and why?

16. Note that $\nu_0(2\text{-}0) < 2\nu_0(1\text{-}0)$ for $H^{79}Br$. Explain the reason for this observation.

17. Compare the values of B_e, B_0 and B_1 for $H^{81}Br$. Explain the reasons for your observation.

18. The following is a common question in placement exams in chemistry graduate schools. "Draw a sketch of the vibration-rotation spectrum of a heteronuclear diatomic molecule (fundamental band only) that has two isotopic species. Identify all special features on this spectrum". Answer this question to the best of your ability.

You are now prepared to publish this work! Well done!!