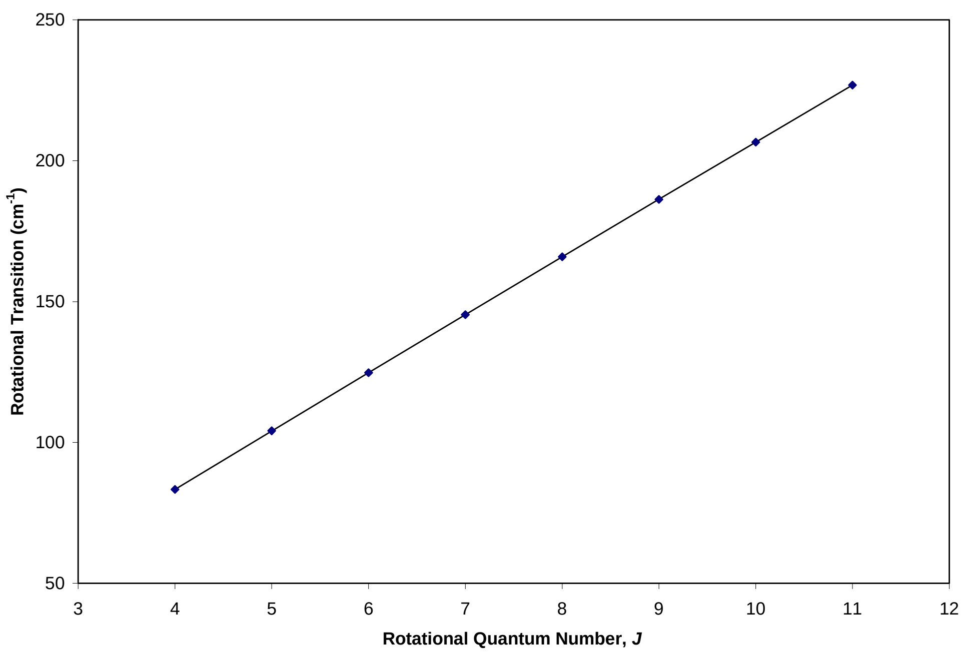
Take-Home Quiz 2
CHEM 325
Spring 2009

Name: ____

1. (10 Points) On the take-home portion of Exam 1 you determined the rotational constant for HCl from the microwave absorption data (given below) assuming that D_J was negligible. Determine D_J, a new value for B and a value for $\tilde{\nu}$ from the data at 95% confidence. Tape a graph showing the data and the best fit line through the data in the space below. Hint: you will need to use an equation that you derived in Post-Exam 1.

Wavenumber (cm^{-1})	83.32	104.13	124.73	145.37	165.89	186.23	206.60	226.86
$J_{initial} \rightarrow J_{final}$	$3 \rightarrow 4$	$4 \rightarrow 5$	$5 \rightarrow 6$	$6 \rightarrow 7$	$7 \rightarrow 8$	$8 \rightarrow 9$	$9 \rightarrow 10$	$10 \rightarrow 11$

The allowed rotational transitions for a linear molecule occur at wavenumbers of $2BJ - 4D_J J^3$ **(from Post-Exam 1). Fitting the data to this equation gives** B = 10.432 ± 0.003 cm^{-1} **and** D_J = 5.1 ± 0.2 x10^{-4} cm^{-1}**, both at 95% confidence (with an RMS error for the fit of 0.04549).**



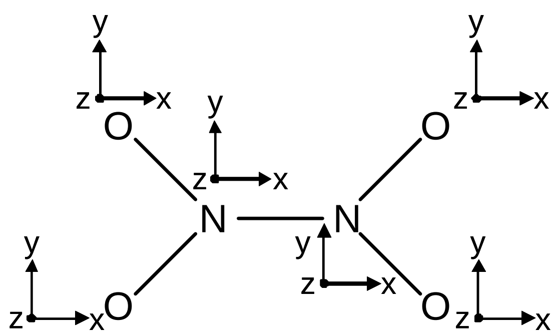
Rearranging the expression for D_J **in terms of** B **and** $\tilde{\nu}$ **(**$D_J = \frac{4B^3}{\tilde{\nu}^2}$**) to solve for** $\tilde{\nu}$

gives $\tilde{\nu} = \sqrt{\frac{4B^3}{D_J}}$ **.**

$$\tilde{\nu} = \sqrt{\frac{4B^3}{D_J}} = \sqrt{\frac{4(10.432\ \text{cm}^{-1})^3}{5.1x10^{-4}\ \text{cm}^{-1}}} = \sqrt{\frac{4541.1_1\ \text{cm}^{-2}}{5.1x10^{-4}}} = 3.0x10^3\ \text{cm}^{-1}$$

Propagation of the uncertainty gives an uncertainty of ±60 cm^{-1}. Since the significant figures analysis indicates that we know $\tilde{\nu}$ to ±100 cm^{-1}, we should go with the more conservative estimate of uncertainty and state $\tilde{\nu} = 3.0 \pm 0.1x10^3\ \text{cm}^{-1}$ at 95% confidence. Note that this is in agreement with the value given in the text for H-^{35}Cl, at least within the number of significant figures that we have in this calculation.

2. (20 Points) Determine the normal modes for N_2O_4. Indicate which modes are IR active and which are Raman active and qualitatively describe the spectrum obtained by each method. Use the coordinate system shown below with the z component of the displacement vector of each atom out of the plane (parallel to the molecular z axis) with the x and y components of the displacement vector in the plane defined by the atoms. Be careful not to confuse the atomic displacement vector components with the molecular axes! I have defined the displacement vector components in such a way so that each is parallel to the corresponding molecular axis.



N_2O_4 has D_{2h} symmetry. Determining how each of the 18 components of the six displacement vectors transform in this point group gives the following reducible representation.

D_{2h}	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)
Γ	18	0	0	-2	0	6	2	0

We now have to reduce this reducible representation to determine the 12 normal modes (3N-6 normal modes for a nonlinear molecule with N = 6). We use the Great Orthogonality Theorem with the order of the group equal to 8. Note that for simplicity the operations which have a character of 0 in the above reducible representation have been omitted in the following calculations.

$$a_{A_g} = \frac{1}{8}[(1)(1)(18) + (1)(1)(-2) + (1)(1)(6) + (1)(1)(2)] = 3$$

$$a_{B_{1g}} = \frac{1}{8}[(1)(1)(18) + (1)(-1)(-2) + (1)(1)(6) + (1)(-1)(2)] = 3$$

$$a_{B_{2g}} = \frac{1}{8}[(1)(1)(18) + (1)(-1)(-2) + (1)(-1)(6) + (1)(1)(2)] = 2$$

$$a_{B_{3g}} = \frac{1}{8}[(1)(1)(18) + (1)(1)(-2) + (1)(-1)(6) + (1)(-1)(2)] = 1$$

$$a_{A_u} = \frac{1}{8}[(1)(1)(18) + (1)(1)(-2) + (1)(-1)(6) + (1)(-1)(2)] = 1$$

$$a_{B_{1u}} = \frac{1}{8}[(1)(1)(18) + (1)(-1)(-2) + (1)(-1)(6) + (1)(1)(2)] = 2$$

$$a_{B_{2u}} = \frac{1}{8}[(1)(1)(18) + (1)(-1)(-2) + (1)(1)(6) + (1)(-1)(2)] = 3$$

$$a_{B_{3u}} = \frac{1}{8}[(1)(1)(18) + (1)(1)(-2) + (1)(1)(6) + (1)(1)(2)] = 3$$

So, Γ = 3 A_g + 3 B_{1g} + 2 B_{2g} + 1 B_{3g} + 1 A_u + 2 B_{1u} + 3 B_{2u} + 3 B_{3u}. Now we remove the rotations (B_{1g} + B_{2g} + B_{3g}) and the translations (B_{1u} + B_{2u} + B_{3u}) to give 3 A_g + 2 B_{1g} + B_{2g} + A_u + B_{1u} + 2 B_{2u} + 2 B_{3u}. Note that, if we add up the character under the operation Ê for each of these irreducible representations, we get 12, as we should because there are 12 normal modes. The selection rule for IR absorbance is that a normal mode must transform the same way as the functions x, y or z, while the selection rule for Raman is that a normal mode must transform as one of the quadratics (any combination of x^2, y^2 and z^2 or xy or xz or yz). We can thus create the following table (if a vibrational transition is allowed there is a + in the table, if the transition is forbidden there is nothing).

	A_g	B_{1g}	B_{2g}	A_u	B_{1u}	B_{2u}	B_{3u}
Raman	+	+	+				
IR					+	+	+

Note that because N_2O_4 has a center of inversion, no mode can be both Raman and IR active. Also note that the A_u mode cannot be excited by light in either Raman or IR spectroscopy (it can be excited by molecular collisions, however). Therefore, the Raman spectrum will consist of 6 transitions (the three A_g normal modes, the two B_{1g} normal modes and a single B_{2g} each at a different wavenumber), while the IR spectrum will consist of 5 transitions (the single B_{1u} normal mode, two B_{2u} normal modes and two B_{3u} normal modes each at a different wavenumber), and none of the peaks that appear in the spectrum with one method will be present in the other method's spectrum.