

**CHEM 325**  
**Spring 2009**  
**Exam 1**

Name: \_\_\_\_\_

**Instructions**

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't assess it and I will assume that you don't know it and will grade your work accordingly.

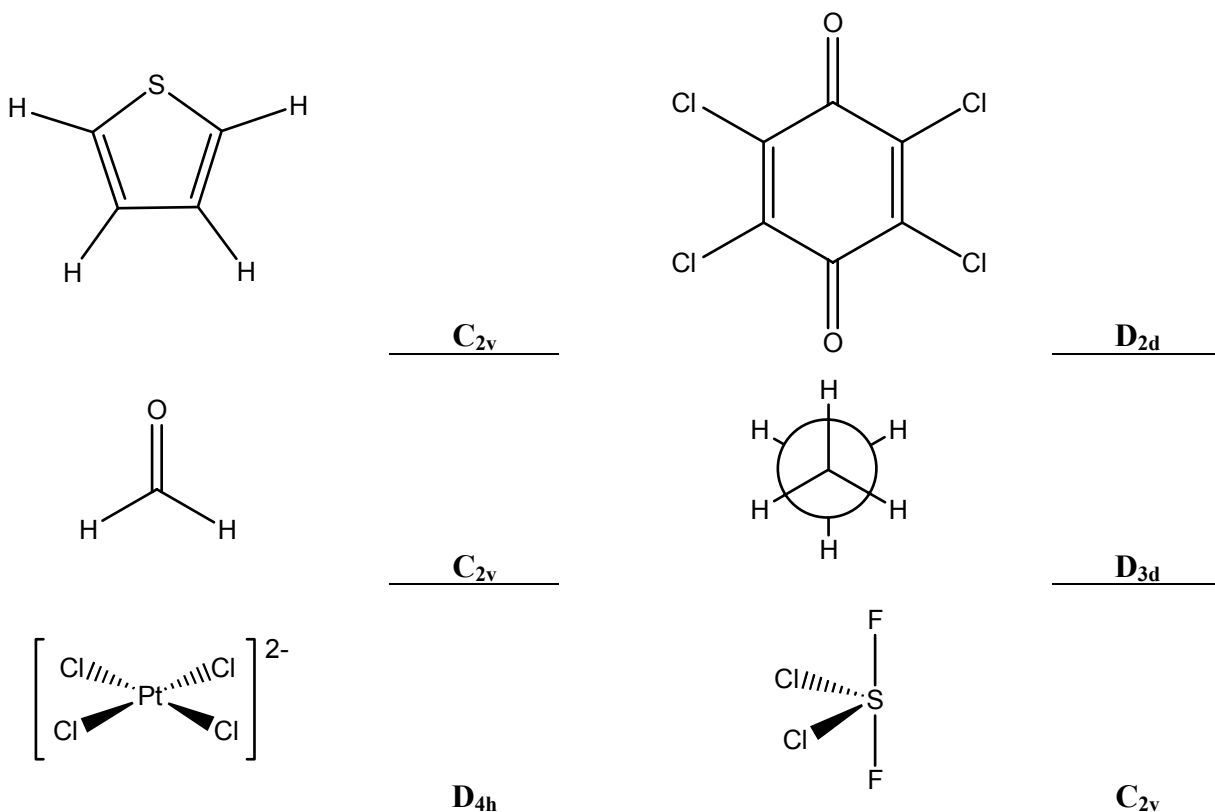
Show all work for full credit! Use complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

There are **9** pages, **0** blank and a separate equation sheet.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received
1	7	
2	4	
3	10	
4	13	
5	10	
6	12	
7	18	
8	11	
Free	15	15
Total	100	
	Bonus	
	Grand Total	

1. (7 Points) Assign the following molecules to the correct point group. Ignore the disposition of any double bonds in aromatic rings.

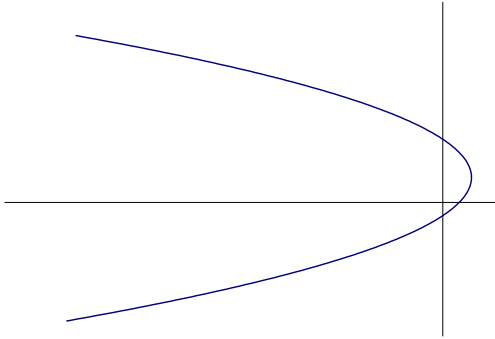


2. (4 Points) Many simple molecules in the gaseous state show a pure rotation spectrum consisting of a series of lines, but in the liquid and solid states the series of lines often collapses to a single broad line. Explain.

**In the liquid state collisional broadening leads to broadened lines that, if severe enough, could lead to a single broad line as all of the rotational transitions that can be observed in the gaseous state overlap each other (in essence the transitions all run together because they are so broad).**

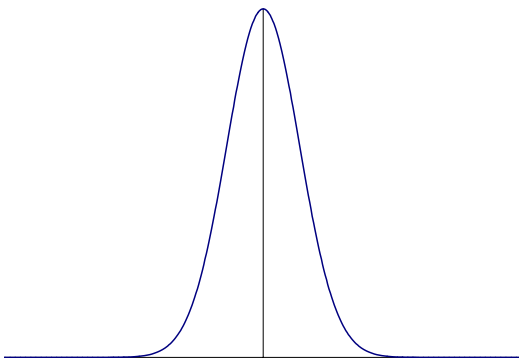
**In both the solid and liquid state the rotor is no longer a free rotor ( $\hat{V}$  in the Hamiltonian no longer equals zero) as a particle could experience a potential caused by all of the other particles surrounding it. As this will vary, depending on a particle's position in the structure and this may change over time (especially in a liquid). In effect every particle would have a different rotational constant, depending on its environment, and instead of having a single set of rotational transitions with a single  $B$ , we would have a large number of overlapping rotational transitions, each with a different  $B$ . If the number of overlapping transitions were large enough then all that would be observed would be a single broad peak corresponding to some average value.**

3. (10 Points) Indicate which of the following functions could, or could not, be a valid quantum mechanical wavefunction. Briefly explain why.



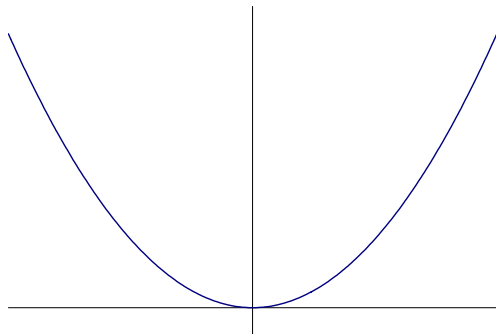
**No good, not single-valued, goes to  $\pm\infty$  as x goes to  $-\infty$ .**

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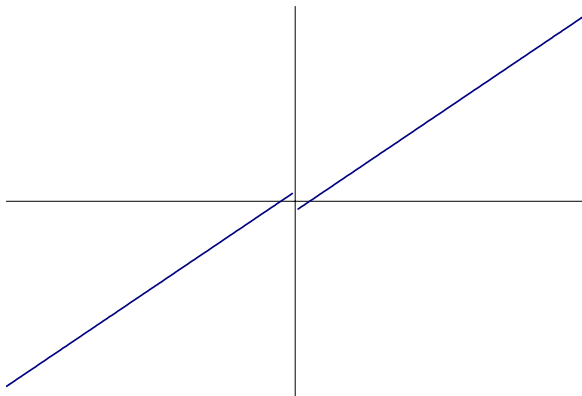
**Good. Continuous, single-valued, continuous first derivative, goes to 0 at  $\pm\infty$ .**

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**No good, goes to  $\pm\infty$  as x goes to  $\pm\infty$ .**

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**No good, discontinuous, first derivative is discontinuous and it goes to  $\pm\infty$  at  $\pm\infty$ .**

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4. Two wavefunctions  $\psi_1$  and  $\psi_2$  are degenerate with respect to the operator  $\hat{M}$ , that is to say  $\hat{M}\psi_1 = m\psi_1$  and  $\hat{M}\psi_2 = m\psi_2$ . We may form a new wavefunction,  $\phi$ , such that  $\phi = c_1\psi_1 + c_2\psi_2$ , where  $c_1$  and  $c_2$  are constants chosen so that  $\phi$  is normalized.

a. (5 Points) Prove that  $\phi$  is an eigenfunction of  $\hat{M}$ .

**To be an eigenfunction the Schrödinger equation ( $\hat{Q}\psi = q\psi$ , where  $\hat{Q}$  is an operator,  $\psi$  is a wavefunction and  $q$  a scalar observable) must be satisfied.**

**Set up the Schrödinger equation for the operator  $\hat{M}$  and distribute the operator through  $\phi$ .**

$$\hat{M}\phi = \hat{M}(c_1\psi_1 + c_2\psi_2) = \hat{M}c_1\psi_1 + \hat{M}c_2\psi_2 = c_1\hat{M}\psi_1 + c_2\hat{M}\psi_2$$

**Since  $\hat{M}\psi_1 = m\psi_1$  and  $\hat{M}\psi_2 = m\psi_2$ , we may write**

$$\hat{M}\phi = c_1m\psi_1 + c_2m\psi_2 = m(c_1\psi_1 + c_2\psi_2) = m\phi$$

**Because the operator  $\hat{M}$  and the wavefunction  $\phi$  satisfy the Schrödinger equation,  $\phi$  is an eigenfunction of  $\hat{M}$  with an eigenvalue of  $m$ .**

b. (4 Points) Determine  $\langle\phi|\hat{M}|\phi\rangle$ .

**We have just shown that  $\hat{M}\phi = m\phi$ , and we know that  $\langle\phi|\phi\rangle = 1$  because the wavefunction is normalized. It, therefore, follows that**

$$\langle\phi|\hat{M}|\phi\rangle = \langle\phi|m|\phi\rangle = m\langle\phi|\phi\rangle = m$$

c. (4 Points) What is the meaning of what you've shown in this problem?

**We may form a linear combination of degenerate eigenfunctions for some operator and that the linear combination is also an eigenfunction of the operator with the same eigenvalue.**

5a. (4 Points) Is the integral  $\iiint (xy)(z)(x^2 - y^2) dx dy dz$  non-zero in  $D_{2d}$  symmetry? Show your work, or give an explanation for full credit.

**To know whether  $\iiint (xy)(z)(x^2 - y^2) dx dy dz$  is non-zero, we only need to consider the triple direct product of the irreducible representations of the functions in the given point group. If the triple direct product contains the totally symmetric representation ( $A_1$  in this case) then the integral is not zero, but if it does not then the integral is zero.**

$$\Gamma_{xy} \times \Gamma_z \times \Gamma_{x^2-y^2} = B_2 \times B_2 \times B_1 = A_1 \times B_1 = B_1$$

**Since the result does not contain  $A_1$ , this integral is zero.**

b. (6 Points) What irreducible representations are spanned by the direct product  $E \times E$  in  $D_{2d}$ ?

$D_{2d}$	E	2 $S_4$	$C_2$	2 $C_2'$	2 $\sigma_d$
E	2	0	-2	0	0
E	2	0	-2	0	0
$E \times E$	4	0	4	0	0

**We know that this direct product must contain  $A_1$ , because of the properties of groups, and we know that if this reducible representation does not contain E, then the only choice we have is that this reducible representation spans all of the other irreducible representations (there is no way to obtain these characters other than using all of the other irreducible representations).**

**Therefore, we use the Great Orthogonality Theorem to determine the number of times that E appears in the reducible representation.**

$$a_E = \frac{1}{8} [(1)(2)(4) + (2)(0)(0) + (1)(-2)(4) + (2)(0)(0) + (2)(0)(0)] = 0$$

**Since E does not appear, we may conclude that  $E \times E = A_1 + A_2 + B_1 + B_2$ .**

*Note that you could have used the Great Orthogonality Theorem to show the same thing.*

$D_{2d}$	E	2 $S_4$	$C_2$	2 $C_2'$	2 $\sigma_d$	
$A_1$	1	1	1	1	1	$x^2+y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$
$B_1$	1	-1	1	1	-1	$x^2-y^2$
$B_2$	1	-1	1	-1	1	$z$
E	2	0	-2	0	0	$(x, y); (R_x, R_y)$ $(xz, yz)$

6a. (6 Points) Demonstrate that the solutions for a two-dimensional quantum mechanical rigid rotor,  $\psi = \frac{1}{\sqrt{2\pi}} e^{im_\ell\phi}$ , with different  $m_\ell$  are orthogonal.

**To be orthogonal  $\langle \psi | \psi \rangle = 0$ . Let one function have  $m_\ell = m$  and the other have  $m_\ell = n$ , where  $m \neq n$ . We can then write the following.**

$$\langle \psi | \psi \rangle = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im\phi} \frac{1}{\sqrt{2\pi}} e^{in\phi} d\phi = \frac{1}{2\pi} \int_0^{2\pi} e^{i(n-m)\phi} d\phi$$

**Using  $e^{i\theta} = \cos\theta + i\sin\theta$  gives  $\langle \psi | \psi \rangle = \frac{1}{2\pi} \int_0^{2\pi} \cos((n-m)\phi) + i\sin((n-m)\phi) d\phi$ . The integral of a sum can be expressed as a sum of integrals, which gives**

$$\langle \psi | \psi \rangle = \frac{1}{2\pi} \left[ \int_0^{2\pi} \cos((n-m)\phi) d\phi + i \int_0^{2\pi} \sin((n-m)\phi) d\phi \right]$$

**The integral of the cosine or the sine function over the interval 0 to  $2\pi$  equals 0, no matter what values of the integers  $n$  and  $m$  we choose. Therefore, the whole expression equals 0, which means that the wavefunctions are orthogonal.**

b. (6 Points) Demonstrate that  $\psi = \frac{1}{\sqrt{2\pi}} e^{im_\ell\phi}$  is an eigenfunction of the operator  $-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$  and determine the eigenvalue.

**For  $\psi$  to be an eigenfunction of the given operator, applying the operator to  $\psi$  must return  $\psi$  multiplied by a constant (the eigenvalue). Apply the operator to the wavefunction.**

$$-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \left( \frac{1}{\sqrt{2\pi}} e^{im_\ell\phi} \right) = \left( -\frac{\hbar^2}{2I} \right) \left( \frac{1}{\sqrt{2\pi}} \right) \frac{\partial^2 e^{im_\ell\phi}}{\partial \phi^2} = (im_\ell)^2 \left( -\frac{\hbar^2}{2I} \right) \left( \frac{1}{\sqrt{2\pi}} \right) e^{im_\ell\phi}$$

$$-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \left( \frac{1}{\sqrt{2\pi}} e^{im_\ell\phi} \right) = \left( \frac{m_\ell^2 \hbar^2}{2I} \right) \psi$$

**Since our criteria for an eigenfunction was met,  $\psi$  is an eigenfunction of the operator and the eigenvalue is  $\frac{m_\ell^2 \hbar^2}{2I}$ .**

7a. (6 Points) In rotational Raman spectroscopy one observes a set of emission lines on either side of an intense line corresponding to the energy of light used to excite the molecules. The selection rule for rotational Raman spectroscopy is  $\Delta J = \pm 2$  and the two sets of observed lines correspond to  $\Delta J = +2$  (the Stokes lines) and  $\Delta J = -2$  (the anti-Stokes lines). Demonstrate that the separation of the Stokes lines (in wavenumbers) is given by the equation  $2B(2J + 3)$ . Assume that each transition starts at a state with a rotational quantum number of  $J$  and ends at a state with a rotational quantum number of  $J + 2$ .

**Start with the term equation for molecular rotations,  $F(J) = BJ(J + 1) - D_J J^2 (J + 1)^2$ , and assume that  $D_J = 0$  so this expression becomes  $F(J) = BJ(J + 1)$ .**

**The allowed Stokes transition is  $J$  to  $J+2$  and the difference in these terms is given by**

$$F(J + 2) - F(J) = B(J + 2)(J + 3) - BJ(J + 1)$$

$$F(J + 2) - F(J) = B(J^2 + 5J + 6) - BJ(J + 1) = BJ^2 + 5BJ + 6B - BJ^2 - BJ$$

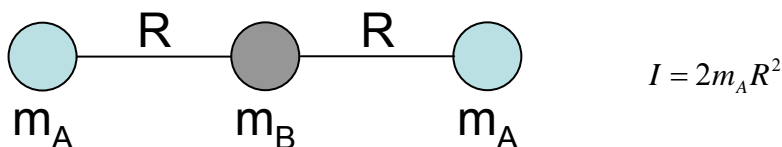
$$F(J + 2) - F(J) = 4BJ + 6B = 2B(2J + 3)$$

**Thus, the allowed rotational transitions with  $\Delta J = +2$  occur at wavenumbers of  $2B(2J + 3)$ .**

b. (4 Points) Rotational Raman spectroscopy can be used to determine the rotational constant of  $\text{CO}_2$ , but pure rotational spectroscopy (i. e., normal rotational spectroscopy) cannot. Explain why  $\text{CO}_2$  does not have a pure rotation spectrum.

**The gross selection rule for rotational spectroscopy is that the molecule must be polar.  $\text{CO}_2$  is a nonpolar molecule, and therefore cannot exhibit a pure rotational spectrum. However, it could still have a rotational spectrum, if there is significant centrifugal distortion (only observable with very long pathlength cells).**

c. (8 Points) The rotational constant for  $^{12}\text{C}-^{16}\text{O}_2$  determined from rotational Raman spectroscopy is  $0.39021\text{ cm}^{-1}$ . Determine the C–O bond length in picometers. The atomic mass of  $^{12}\text{C}$  is 12.0000 amu and the atomic mass of  $^{16}\text{O}$  is 15.9949 amu.



Start with the expressions for  $B$  and  $I$  and solve for  $R$ .

$$B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{8\pi c m_A R^2}$$

$$R^2 = \frac{\hbar}{8\pi c m_A B}$$

$$R = \sqrt{\frac{\hbar}{8\pi c m_A B}}$$

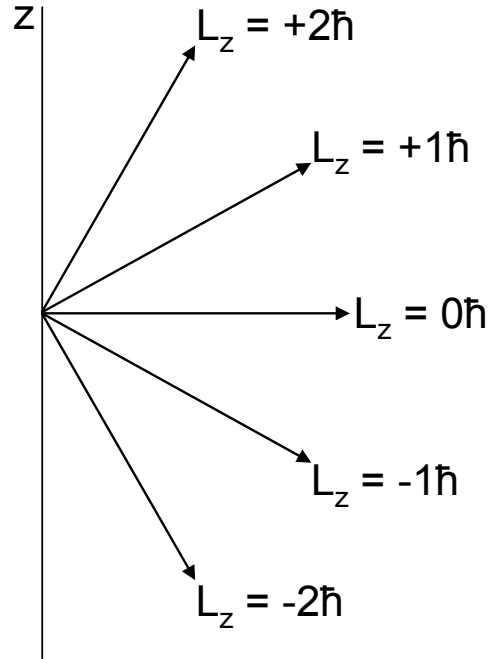
$$R = \sqrt{\frac{1.05457 \times 10^{-34} \text{ J}\cdot\text{s}}{8\pi (2.99792458 \times 10^{10} \text{ cm}\cdot\text{s}^{-1})(15.9949 \text{ amu}) \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) (0.39021 \text{ cm}^{-1})}}$$

$$R = \sqrt{\frac{1.05457 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}\cdot\text{s}}{7.8087_1 \times 10^{-15} \text{ kg}\cdot\text{s}^{-1}}} = \sqrt{1.3505_0 \times 10^{-20} \text{ m}^2} = 1.1621_1 \times 10^{-10} \text{ m}$$

$$R = 1.1621_1 \times 10^{-10} \text{ m} \left( \frac{1 \text{ pm}}{1 \times 10^{-12} \text{ m}} \right) = 116.21 \text{ pm}$$

The C–O bond length in  $\text{CO}_2$  is 116.21 pm.

8. (8 Points) Draw a vector representation, using arrows to show the direction of the angular momentum vectors, of a rigid rotor's allowed orientations when  $\ell = 2$ . Indicate the magnitude of each vector and the different values of  $L_z$  on your picture.



All have  $\ell = 2$ , and so they all have the same magnitude,  
 $|\vec{L}| = \sqrt{\ell(\ell+1)}\hbar = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ .

b. (3 Points) Why is the vector representation more properly shown as cones, instead of arrows?

The operators  $\hat{l}_x$ ,  $\hat{l}_y$  and  $\hat{l}_z$  do not commute with each other, but they do commute with the  $\hat{l}$ . Therefore, we can know  $\hat{l}$  and one of its components, but not the other two. Since, by convention, we choose to know  $\hat{l}_z$  the other components of the vector are undefined. To more properly show the uncertainty in the values of  $\hat{l}_x$  and  $\hat{l}_y$ , we would show the vectors as cones to indicate that the angular momentum vector can be anywhere on the cone.

### Additional Problems from the Post-Exam

S1. Is the transition from a state with  $A_1$  symmetry to a state with  $A_2$  symmetry electric dipole allowed in  $C_{2v}$  symmetry? If it is allowed, in what polarization is it allowed?

**In  $C_{2v}$ , the electric dipole operator transforms as  $A_1$  (z),  $B_1$  (x) and  $B_2$  (y). To be allowed in one of these polarizations the triple direct product  $A_2 \times \Gamma_\mu \times A_1$  must contain  $A_1$ . Since  $A_1 \times A_2 = A_2$ , the only way that this transition can be allowed is if  $\Gamma_\mu$  is  $A_2$ . None of the components of the electric dipole operator transforms as  $A_2$ , therefore this transition is forbidden.**

S2a. Determine the equation in terms of  $J$  and  $J-1$  that gives the splitting between the allowed molecular rotational transitions for a linear molecule when the centrifugal distortion is not zero.

**Start with the expression for the rotational terms:  $F(J) = BJ(J+1) - D_J J^2(J+1)^2$ . The difference between these terms, corresponding to the allowed rotational transitions is then**

$$F(J) - F(J-1) = BJ(J+1) - D_J J^2(J+1)^2 - B(J-1)J + D_J (J-1)^2(J)^2$$

$$F(J) - F(J-1) = BJ(J+1) - B(J-1)J + D_J (J-1)^2(J)^2 - D_J J^2(J+1)^2$$

$$F(J) - F(J-1) = BJ[(J+1) - (J-1)] + D_J J^2[(J-1)^2 - (J+1)^2]$$

$$F(J) - F(J-1) = 2BJ + D_J J^2[J^2 - 2J + 1 - (J^2 + 2J + 1)]$$

$$F(J) - F(J-1) = 2BJ + D_J J^2[-2J - 2J] = 2BJ - 4D_J J^3$$

**The allowed rotational transitions for a linear molecule occur at wavenumbers of  $2BJ - 4D_J J^3$ .**

b. Given that the spacing of the lines in the rotational spectrum of  $^{35}\text{Cl}^{19}\text{F}$  is  $1.033\text{ cm}^{-1}$  and the isotopic masses are  $34.968853\text{ amu}$  for  $^{35}\text{Cl}$  and  $18.99840\text{ amu}$  for  $^{19}\text{F}$ , what is the Cl–F bond length in  $^{35}\text{Cl}^{19}\text{F}$  in picometers?

**As the peak splittings are constant, we may conclude that  $D_J$  is 0 for this molecule. If  $D_J$  is zero, then the peaks will occur at  $2B$ ,  $4B$ ,  $6B$ , etc. with a splitting between lines of  $2B$ . This means that  $B = 0.5165\text{ cm}^{-1}$ .**

**Solve  $B = \frac{\hbar}{4\pi cI}$  for  $I$  to give  $I = \frac{\hbar}{4\pi cB}$ . Substituting into  $I = \mu r^2$  and simplifying gives**

$$r = \left( \frac{\hbar}{4\pi cB\mu} \right)^{1/2} = \left( \frac{h}{8\pi^2 cB\mu} \right)^{1/2}.$$

**Determine  $\mu$ .**

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(34.968853\text{ amu})(18.99840\text{ amu})}{34.968853\text{ amu} + 18.99840\text{ amu}} = \frac{664.3522_5}{53.96725_3}\text{ amu} = 12.31028_5\text{ amu}$$

**Convert to kg.**

$$\mu = 12.31028_5\text{ amu} \left( \frac{1.66054 \times 10^{-27}\text{ kg}}{1\text{ amu}} \right) = 2.04417_2 \times 10^{-26}\text{ kg}$$

**Substitute in known quantities and solve for  $r$ .**

$$r = \left( \frac{6.62608 \times 10^{-34}\text{ J}\cdot\text{s}}{8\pi^2 (2.99792458 \times 10^{10}\text{ cm}\cdot\text{s}^{-1})(0.5165\text{ cm}^{-1})(2.04417_2 \times 10^{-26}\text{ kg})} \right)^{1/2}$$

$$r = \left( \frac{6.62608 \times 10^{-34}\text{ J}\cdot\text{s}}{2.499_1 \times 10^{-14}\text{ kg}\cdot\text{s}^{-1}} \right)^{1/2} = (2.651_2 \times 10^{-20}\text{ m}^2)^{1/2} = 1.628 \times 10^{-10}\text{ m} = 162.8\text{ pm}$$

**The Cl–F bond length is 162.8 pm (1.628 Å).**

c. Calculate  $B$  for  $^{37}\text{Cl}^{19}\text{F}$ .

To find  $B$  for  $^{37}\text{Cl}^{19}\text{F}$ , first combine  $B = \frac{\hbar}{4\pi c I}$  and  $I = \mu r^2$  to give  $B = \frac{h}{8\pi^2 c \mu r^2}$ .

Determine  $\mu$  using the isotopic mass of  $^{37}\text{Cl}$  (36.965903 amu).

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(36.965903 \text{ amu})(18.99840 \text{ amu})}{36.965903 \text{ amu} + 18.99840 \text{ amu}} = \frac{702.2930_1}{55.96430_3} \text{ amu} = 12.54894_6 \text{ amu}$$

Convert to kg.

$$\mu = 12.54894_6 \text{ amu} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) = 2.08380_3 \times 10^{-26} \text{ kg}$$

Substitute in, noting that  $r$  is the same as in part  $b$ , and solve.

$$B = \frac{h}{8\pi^2 c \mu r^2} = \frac{6.62608 \times 10^{-34} \text{ J} \cdot \text{s}}{8\pi^2 (2.99792458 \times 10^8 \text{ m} \cdot \text{s}^{-1}) (2.08380_3 \times 10^{-26} \text{ kg}) (1.628 \times 10^{-10} \text{ m})^2}$$
$$B = \frac{6.62608 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \cdot \text{s}}{1.307_3 \times 10^{-35} \text{ kg} \cdot \text{m}^3 \cdot \text{s}^{-1}} = 50.69 \text{ m}^{-1}$$

Convert to wavenumbers.

$$B = 50.69 \text{ m}^{-1} \left( \frac{0.0100 \text{ cm}^{-1}}{1 \text{ m}^{-1}} \right) = 0.5069 \text{ cm}^{-1}$$

$B$  for  $^{37}\text{Cl}^{19}\text{F}$  is  $0.5069 \text{ cm}^{-1}$ .

d. Will the rotational transitions of  $^{37}\text{Cl}^{19}\text{F}$  occur at higher, at lower, or at the same wavenumbers as those of  $^{35}\text{Cl}^{19}\text{F}$ ?

The reduced mass of  $^{37}\text{Cl}^{19}\text{F}$  is larger than that of  $^{35}\text{Cl}^{19}\text{F}$ , therefore  $I$  is also larger ( $r$  is the same for both). A larger  $I$  means that  $B$  is smaller for  $^{37}\text{Cl}^{19}\text{F}$  and the peaks occur at lower wavenumbers than those of  $^{35}\text{Cl}^{19}\text{F}$ .

S3. The threshold frequency for the emission of a photoelectron from Na metal is  $43.9 \times 10^{13} \text{ s}^{-1}$ . What is the ionization energy of Na in kJ/mole?

**At the threshold frequency light has just enough energy of promote an electron from its lowest energy state to the continuum (the lowest unbound state with a kinetic energy of 0). We can start with the equation for the photoelectric effect,**

$$\frac{1}{2}mv^2 = h\nu - \Phi, \text{ set } v = 0 \text{ and solve for } \Phi \text{ to give } \Phi = h\nu.$$

$$\Phi = h\nu = (6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(43.9 \times 10^{13} \text{ s}^{-1}) = 2.90_8 \times 10^{-19} \text{ J}$$

$$\frac{2.90_8 \times 10^{-19} \text{ J}}{1 \text{ molecule}} \left( \frac{6.02214 \times 10^{23} \text{ molecule}}{1 \text{ mole}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 175. \text{ kJ/mole}$$

**The ionization energy of Na metal should be 175. kJ/mole.**

S4. Given that the Br-Br bond distance is 283.3 pm, what must a spectrometer's resolution be (in  $\text{cm}^{-1}$ ) to distinguish between the Stokes lines arising from the  $^{79}\text{Br}-^{81}\text{Br}$ ,  $^{79}\text{Br}-^{79}\text{Br}$  and  $^{81}\text{Br}-^{81}\text{Br}$  isotopomers in a rotational Raman spectrum? Assume that the resolution must be half of the smallest splitting that you seek to measure.

**From question 7a, we know that the wavenumber of a transition in rotational Raman spectroscopy is given by the equation  $F(J+2) - F(J) = 2B(2J+3)$ .**

**The isotopic mass of  $^{79}\text{Br}$  is 78.9183 amu while the isotopic mass of  $^{81}\text{Br}$  is 80.9163 amu.**

**The reduced mass of  $^{79}\text{Br}-^{79}\text{Br}$  is**

$$\mu = \frac{(78.9183 \text{ amu})^2}{2(78.9183 \text{ amu})} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) = \frac{(78.9183 \text{ amu})}{2} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = 6.55235_0 \times 10^{-26} \text{ kg}$$

**The reduced mass of  $^{79}\text{Br}-^{81}\text{Br}$  is**

$$\mu = \frac{(78.9183 \text{ amu})(80.9163 \text{ amu})}{(78.9183 \text{ amu} + 80.9163 \text{ amu})} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = \frac{(6385.77_6) \text{ amu}}{159.8346} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = 39.9524_0 \text{ amu} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) = 6.63425_7 \times 10^{-26} \text{ kg}$$

The reduced mass of  $^{81}\text{Br}-^{81}\text{Br}$  is

$$\mu = \frac{(80.9163 \text{ amu})^2}{2(80.9163 \text{ amu})} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right) = \frac{(80.9163 \text{ amu})}{2} \left( \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)$$

$$\mu = 6.71823_8 \times 10^{-26} \text{ kg}$$

Now we calculate  $B$  for each of the isotopomers using  $B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c \mu r^2}$ .

For  $^{79}\text{Br}-^{79}\text{Br}$   $B$  is

$$B = \frac{\hbar}{4\pi c \mu r^2} = \frac{1.05457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{4\pi (2.99792458 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}) (6.55235_0 \times 10^{-26} \text{ kg}) (283.3 \times 10^{-12} \text{ m})^2}$$

$$B = 0.05323 \text{ cm}^{-1}$$

For  $^{79}\text{Br}-^{81}\text{Br}$   $B$  is

$$B = \frac{\hbar}{4\pi c \mu r^2} = \frac{1.05457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{4\pi (2.99792458 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}) (6.63425_7 \times 10^{-26} \text{ kg}) (283.3 \times 10^{-12} \text{ m})^2}$$

$$B = 0.05257 \text{ cm}^{-1}$$

For  $^{81}\text{Br}-^{81}\text{Br}$   $B$  is

$$B = \frac{\hbar}{4\pi c \mu r^2} = \frac{1.05457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{4\pi (2.99792458 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}) (6.71823_8 \times 10^{-26} \text{ kg}) (283.3 \times 10^{-12} \text{ m})^2}$$

$$B = 0.05192 \text{ cm}^{-1}$$

The first transitions are (this is the  $J = 0$  to  $J = 2$  transition, so we use  $J = 0$  in our term equation  $2B(2J + 3) = 6B$ ):

$$^{79}\text{Br}-^{79}\text{Br}: 6B = 0.3193_8 \text{ cm}^{-1}$$

$$^{79}\text{Br}-^{81}\text{Br}: 6B = 0.3154_2 \text{ cm}^{-1}$$

$$^{81}\text{Br}-^{81}\text{Br}: 6B = 0.3115_2 \text{ cm}^{-1}$$

The difference between these peaks is approximately  $0.0039 \text{ cm}^{-1}$  ( $0.0039_6 \text{ cm}^{-1}$  for  $^{79}\text{Br}-^{79}\text{Br}$  and  $^{79}\text{Br}-^{81}\text{Br}$  and  $0.0039_0 \text{ cm}^{-1}$  for  $^{79}\text{Br}-^{81}\text{Br}$  and  $^{81}\text{Br}-^{81}\text{Br}$ ), which means our spectrometer would need to have a resolution of about  $0.0020 \text{ cm}^{-1}$  to be able to distinguish between these isotopomers.

S5. Naphthalene may be approximated as a  $4.00 \text{ \AA} \times 7.00 \text{ \AA}$  rectangular box. Calculate the expected wavenumber for the light absorbed to give the first excited state of naphthalene.

The equation for a two-dimensional rectangular box is  $E_{n_x, n_y} = \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{h^2}{8m}$ . Let

$L_x = 4.00 \times 10^{-10} \text{ m}$  and  $L_y = 7.00 \times 10^{-10} \text{ m}$ . The lowest energy level in naphthalene has  $n_x = n_y = 1$  and the next lowest state will have  $n_x = 1$  and  $n_y = 2$ .

$$E_{1,1} = \left( \frac{1}{(4.00 \times 10^{-10} \text{ m})^2} + \frac{1}{(7.00 \times 10^{-10} \text{ m})^2} \right) \frac{(6.62608 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})^2}{8(9.10938 \times 10^{-31} \text{ kg})}$$

$$E_{1,1} = (8.29_0 \times 10^{18}) (6.02468_8 \times 10^{-38}) \text{ J} = 4.99_4 \times 10^{-19} \text{ J} \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) = 2.51_4 \times 10^4 \text{ cm}^{-1}$$

$$E_{1,2} = \left( \frac{1}{(4.00 \times 10^{-10} \text{ m})^2} + \frac{4}{(7.00 \times 10^{-10} \text{ m})^2} \right) \frac{(6.62608 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})^2}{8(9.10938 \times 10^{-31} \text{ kg})}$$

$$E_{1,2} = (1.44_1 \times 10^{19}) (6.02468_8 \times 10^{-38}) \text{ J} = 8.68_3 \times 10^{-18} \text{ J} \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) = 4.37_1 \times 10^4 \text{ cm}^{-1}$$

Note that the  $n_x = 2, n_y = 1$  state has an energy of  $6.96 \times 10^4 \text{ cm}^{-1}$ .

The transition between the ground state and the excited state should occur at an energy of  $E_{1,2} - E_{1,1} = (4.37_1 \times 10^4 - 2.51_4 \times 10^4) \text{ cm}^{-1} = 1.85_7 \times 10^4 \text{ cm}^{-1}$ . This transition is predicted to occur at  $1.86 \times 10^4 \text{ cm}^{-1}$  (538. nm).

$$E_{1,2} = \left( \frac{4}{(4.00 \times 10^{-10} \text{ m})^2} + \frac{1}{(7.00 \times 10^{-10} \text{ m})^2} \right) \frac{(6.62608 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1})^2}{8(9.10938 \times 10^{-31} \text{ kg})}$$

$$E_{1,2} = (2.70_4 \times 10^{19}) (6.02468_8 \times 10^{-38}) \text{ J} = 1.62_9 \times 10^{-18} \text{ J} \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) = 8.20_1 \times 10^4 \text{ cm}^{-1}$$

S6. The lowest-lying excited state of a molecule is  $15.0 \text{ cm}^{-1}$  above the ground state in energy. To what temperature, in K, must a sample of this molecule be cooled so that 90.0% of the molecules in the sample are in the ground state? Assume both states are singly degenerate.

Start with the Boltzmann equation  $\frac{N_i}{N} = \frac{g_i e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}}$ , which in our case will be simply

$\frac{N_i}{N} = \frac{e^{-E_i/kT}}{e^{-E_0/kT} + e^{-E_1/kT}}$  (since  $g = 1$  for both states). For simplicity, we will let the energy of the ground state,  $E_0$ , equal  $0.00 \text{ cm}^{-1}$  and so the energy of the excited state,  $E_1$ , equals  $15.0 \text{ cm}^{-1}$ . Substituting gives

$$\frac{e^{-0/kT}}{e^{-0/kT} + e^{-15.0/kT}} = 0.900$$

$$\frac{1}{1 + e^{-15.0/kT}} = 0.900$$

$$1 = 0.900(1 + e^{-15.0/kT})$$

$$e^{-15.0/kT} = \frac{1}{0.900} - 1 = 0.111_1$$

$$\frac{-15.0 \text{ cm}^{-1}}{kT} = \ln(0.111_1) = -2.19_7$$

$$T = \frac{15.0 \text{ cm}^{-1}}{2.19_7 k} = \frac{15.0 \text{ cm}^{-1}}{2.19_7 (1.38065 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \left( \frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right)} = 9.82 \text{ K}$$

The sample must be cooled to **9.82 K** to have **90.0%** of the molecules in the ground state.