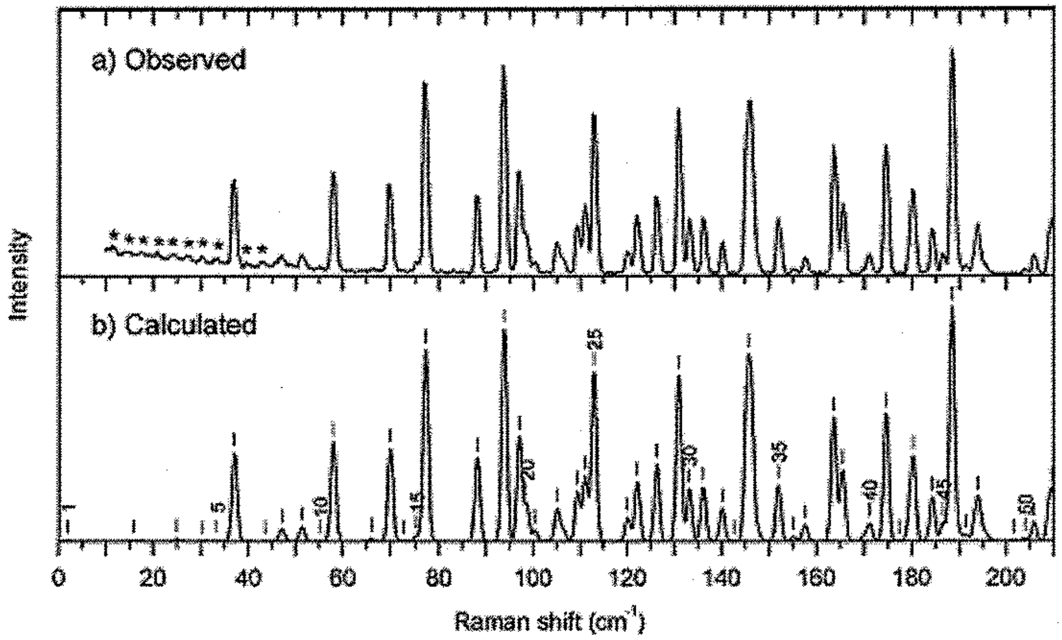
Physical Chemistry
Cumulative Exam
October 2, 2003
Cynthia J. Jameson

This exam uses the rovibrational spectroscopy of water molecule: H_2O, HDO and D_2O as the basis for inquiring about your knowledge of symmetry (group theory), internal degrees of freedom of a molecule, molecular spectroscopy, quantum mechanics, partition functions, angular momentum, Pauli exclusion principle, in other words, basic, fundamental physical chemistry. The references are not a required reading for these problems. They are given herein only for your future enlightenment, should you wish a more complete treatment than you are able to do by yourself in this exam.

In spite of the relevance of water as one of the most ubiquitous and abundant molecules in nature, the rotational Raman spectrum of H_2O in the vapor phase was reported as late as 1977 and the D_2O and HDO not until ***August 2003*** [G. Avila, et al. *J. Molec. Spectrosc.* 220 (2003) 259-275]. The D_2O and HDO line positions and strengths have been collected by Fourier Transform spectroscopy in the 600-3100 cm^{-1} range and reported by R. A. Toth in May 1999 [*J. Molec. Spectrosc.* 195 (1999) 73, 98]. The molecule has been studied and used extensively as an example in Herzberg's Infrared and Raman Spectra and many other textbooks. A piece of the rotational Raman spectrum (Avila et al., 2003) is shown below:



Rotational Raman spectrum of H_2O p = 23 mbar, at 294 K recorded at 90° scattering geometry using linearly polarized 514.5 nm provided by an Ar$^+$ laser. Ignore the CO_2 impurity lines (*).

For uniformity, use the reference axis system and character table shown below.

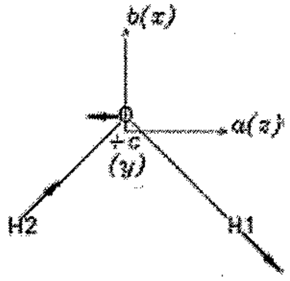


FIG. 1. Reference axis systems and phase of the vibrational coordinate q_3 of H_2O (vibrational displacements not drawn to scale).

TABLE 1 (consult Fig. 1 for axes)

C_{2v}	E	C_2	σ_{ab} or σ_{zx}	σ_{bc} or σ_{xy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

In what follows, you will neglect vibrational-rotational interaction terms in the Hamiltonian.

Questions:

1. ***Determine*** the number of vibrational degrees of freedom for H_2O and D_2O. ***Classify*** each vibrational mode according to the irreducible representations of the point group.

2. One of the vibrational symmetry coordinates is shown in the Fig.1. Copy the same axis system and this symmetry coordinate. ***Draw*** the remaining vibrational symmetry coordinates. Attach a symmetry species label to each, (including the one in Fig. 1) and number the symmetry coordinates according to standard convention. ***Express*** each of the symmetry coordinates in terms of the internal displacement coordinates Δr_1, Δr_2, $d\Delta\phi$, where $d = 1$ Å is a normalization length.

3. ***Determine*** the symmetry force constants that you would need in order to set up the solutions to the vibrational problem. ***Define*** each in terms of the appropriate derivatives. Be sure to define the symbols you use, even if they are standard symbols.

4. The ground vibrational state is totally symmetric, of course. ***Explain*** why. ***Classify*** the lowest 4 vibrational states of H_2O according to symmetry species.

5. ***Classify*** the H_2O or D_2O molecule according to rotation: spherical top, symmetric top or asymmetric top, which one? Of the inertial axes (a, b, c) shown coincident with Cartesian z, x, and y axes, ***determine which one*** corresponds to the largest moment of inertia. ***Which one*** corresponds to the largest rotational

constant? Are the answers the same for D_2O as for H_2O? ***What*** are the quantum numbers for the rotational states of H_2O? ***Which ones*** do the rotational energies depend on? ***State the conditions*** that relate the quantum numbers to each other. On this basis, ***determine*** the degeneracy associated with J = 0, also J = 2.

6. There is an additional source of degeneracy, the nuclear spin statistical weight. For $H_2{}^{16}O$ it is 1 and 3, for $D_2{}^{16}O$ it is 6 and 3. ***Derive*** these nuclear spin statistical weights, keeping in mind the general statement of the Pauli exclusion principle with respect to the TOTAL WAVEFUNCTION and permutation of any two indistinguishable particles.

7. Raman spectroscopy depends on the electric dipole polarizability tensor α (a function of nuclear coordinates) for the molecule. ***Classify*** each of the tensor components according to symmetry species. [Hint: You need to recall the second order perturbation theory expression that is used to calculate α.] Organize your answers by copying TABLE 1 and placing each of the tensor components into the row of the appropriate symmetry species.

8. Make use of group theory (use TABLE 1) to ***determine*** the rotational selection rules for the vibrational bands of H_2O by completing the following table (TABLE 2). NOTE : The rows are not the same order as TABLE 1, on purpose. You have to figure out from the odds and evens which symmetry species in TABLE 1 go with each row in TABLE 2 below:

Symmetry species of vibration	Components of the polarizability tensor	Rotational selection rules in K_a and K_c use these!		Allowed transitions (You do not need to know what is below in this column; given just for completeness)
		ΔK_a	ΔK_c	
		odd	even	ee↔oe, eo↔oo
		odd	odd	ee↔oo, eo↔oe
		even	even	ee↔ee,oo↔oo,eo↔eo,oe↔oe
		even	odd	ee↔eo, oe↔oo

9. According to the polarizability theory of the Raman effect, the differential scattering cross section for a transition $i \rightarrow f$ between two rovibrational states $|i\rangle$ and $|f\rangle$, of energies E_i and E_f, for a gaseous sample at thermal equilibrium, is given in the SI system as

$$(\pi/\varepsilon_0)^2 \bullet (\nu_0-\nu)^4 \bullet w_i \bullet \exp[-E_i/k_BT]/Z(T) \bullet |\langle f \mid \alpha_{MN} \mid i\rangle|^2.$$

where ε_0 is the permittivity of the vacuum; ν_0 is the wavenumber of the exciting light; $\nu = (E_f - E_i)/hc$, the wavenumber of the Raman shift; w_i is the nuclear spin statistical weight of the initial state of the transition; $Z(T)$ is the total partition function at T; and $\langle f |\alpha_{MN}| i\rangle$ the transition moment of the MN Cartesian component in the space-fixed axis of the polarizability tensor for the electronic ground state. ***Explain*** how each term (separated by •) arises to determine the spectral intensity.

10. For gaseous samples it is necessary to average the term $|\langle f \mid \alpha_{MN} \mid i\rangle|^2$ over all possible orientations of the molecule. ***Explain why***. Furthermore, the expression above has to be added up over all values of the magnetic quantum

number *m* of initial and final states contributing to the same frequency. ***Explain why***. After averaging over all spatial orientations the part due to the trace (of the polarizability $\alpha^{(0)}$ and the part due to the anisotropy of the polarizability tensor $\alpha^{(2)}$, the contributions appear with different ratios (also determined by group theory), depending on the scattering geometry: parallel polarization (M=N) and perpendicular polarization (M≠N). For example, for parallel polarization for when transition $i \to f$ is $VR \to V'R'$, we have scattering strengths weighted as follows:

$$(1/3)\,|\langle V'R'|\,\alpha^{(0)}\,|VR\rangle|^2 + (2/15)\,|\langle V'R'|\,\alpha^{(2)}\,|VR\rangle|^2$$

V and *R* of course stand for the set of vibrational and rotational quantum numbers, respectively. ***Give two examples*** of *V* for the H_2O molecule.

11. ***Express*** the partition function Z(T) for the H_2O molecule in terms of these quantum numbers. You will need the degeneracies arrived at in question 5.

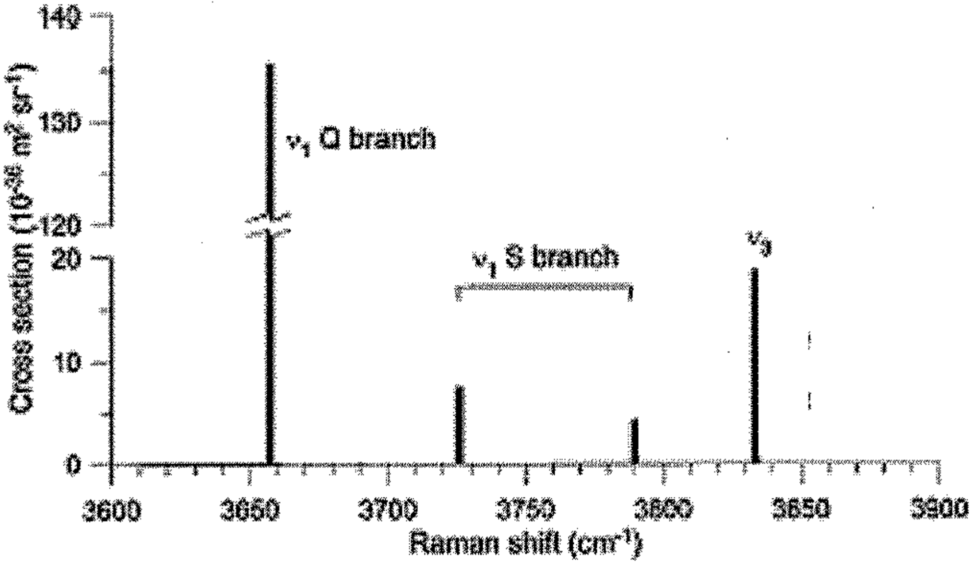
12. Since α is a function of nuclear coordinates, we expand it (applies to each of the components) in a Taylor series in the dimensionless normal coordinates q_j of the molecule:

$$\alpha = \alpha_{\text{equil}} + \sum_j (\partial\alpha/\partial q_j)_{\text{equil}}\, q_j + \ldots$$

By symmetry, ***determine which*** are the only non-vanishing first derivatives of α. [Hint: Consult your answers to questions 1 and 7 to answer this question.] These are the molecular quantities that are used to calculate the intensities of the Raman spectrum of H_2O.

13. Based on your answer to question 10, in the harmonic approximation, ***determine*** which of the $\langle V'|\,\alpha\,|V\rangle$ are non-vanishing by symmetry.

14. The predicted Raman spectrum of water vapor in the OH stretching region at T = 3 K is shown below (Avila et al., 1999). At this temperature the spectrum is striking because only four transitions will be observed, in accordance with the selection rules you have considered above. Using your answer to question 11, ***explain why*** only four lines. ***Associate each line*** with the appropriate initial and final states (rotational and vibrational quantum numbers).



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Answers: (These answers are very detailed for the student's benefit.)

1. There are 3 degrees of freedom for each atom, so a total of 9, of which 3 are translation and 3 are rotation. The translation are given by the symmetry species of x,y,z which are easily classified (results shown below) by looking at Fig. 1 and TABLE 1. Also rotations are classified in the same way (results shown below):

TABLE 1 (consult Fig. 1 for axes)

C_{2v}	E	C_2	σ_{ab} or σ_{zx}	σ_{bc} or σ_{xy}	
A_1	1	1	1	1	x
A_2	1	1	-1	-1	R_x
B_1	1	-1	1	-1	z, R_y
B_2	1	-1	-1	1	y, R_z

Place three Cartesian displacement vectors at each of H_1, H_2, and O to serve as the basis for a 9x9 reducible representation. We need only the trace or character for each of the classes (here each symmetry operation is in a class by itself in this group of order 4). Looking only at the contributors to the trace,
we obtain Γ_{Cart} by taking
(1/4)[sum over $\chi_{Cart} \bullet \chi_{A1}$ for each symmetry operation],
to find how many times A_1 is contained in Γ_{Cart}. Do the others the same way.

C_{2v}	E	C_2	σ_{zx}	σ_{xy}	how many
Γ_{Cart}	9	-1	3	1	
A_1	1	1	1	1	3
A_2	1	1	-1	-1	1
B_1	1	-1	1	-1	3
B_2	1	-1	-1	1	2

$\Gamma_{Cart} = 3A_1 + A_2 + 3B_1 + 2B_2 = \Gamma_{Vibr} + \Gamma_{Trans} + \Gamma_{Rot}$
$\Gamma_{Trans} = A_1 \quad + B_1 + B_2$
$\Gamma_{Rot} = \quad A_2 + B_1 + B_2$

$\Gamma_{Vibr} = 2A_1 \quad + B_1$ that is, two vibrational modes are A_1 the third is B_1.

2. The asymmetric one, q_3, the asymmetric OH stretch, is the one given in Fig. 1. The first two must belong to A_1; clearly we need a symmetric stretch and an angle deformation. Standard convention names the totally symmetric modes first and makes the symmetric stretch q_1; which means the angle deformation is q_2. The symmetry coordinates are therefore:

$S_1(A_1) = (\Delta r_1 + \Delta r_2)/\sqrt{2}$; $S_2(A_1) = d\Delta\phi$; $S_3(B_1) = (\Delta r_1 - \Delta r_2)/\sqrt{2}$,

3. The symmetry force constants are the second derivatives of the potential energy with respect to the symmetry coordinates. Because each term in the expansion of V has to be totally symmetric, there can be no terms in S_iS_j where i and j do not belong to the same irreducible representation. For such terms to not exist, the derivatives (the coefficients in front of S_iS_j in the series expansion of V) that mix symmetry species A_1 and B_1 must vanish. We can have terms in S_1^2, S_2^2, S_3^2, and S_1S_2; S_1S_3 and S_2S_3 can not exist. The non-zero symmetry force constants are $F_{11} = \partial^2V/\partial S_1^2$, $F_{12} = \partial^2V/\partial S_1\partial S_2$, $F_{22} = \partial^2V/\partial S_2^2$, $F_{33} = \partial^2V/\partial S_3^2$. There are no others.

4. Since each one of the vibrations is non-degenerate (A_1 and B_1 are one-dimensional representations) then there is only one vibrational quantum number to characterize each mode: $|v_1v_2v_3\rangle$. Thus the ground state is $|000\rangle$, the fundamentals are $|100\rangle$, $|010\rangle$, $|001\rangle$, overtone states are $|020\rangle$, $|011\rangle$, for example. We obtain the symmetry species from the product of the three symmetry species.

state	symmetry species
$\|000\rangle$	A_1
$\|010\rangle$	A_1
$\|100\rangle$	A_1
$\|001\rangle$	B_1
$\|020\rangle$	A_1
$\|110\rangle$	A_1
$\|011\rangle$	B_1
$\|002\rangle$	A_1

5. H_2O and D_2O are asymmetric tops since no two moments of inertia are equal. The moment of inertia is defined by the sum over $m_ir_i^2$ where r_i is the distance of the mass m_i from the inertial axis. (See Fig. 1) The smallest moment is with respect to the x axis (since no oxygen contribution to this one). The largest moment is with respect to the y axis. The largest rotational constant is $\hbar^2/2I_x$. The same for D_2O; the moments are different (D has larger mass) but the relative order is the same as for H_2O.

The quantum numbers for rotation are J, K, m, with the energies depending on J and K for a symmetric top. Energy levels are (2J+1)-degenerate with respect to m, m=0, ±1, ±2, ±3, …±J, unless the top is in a magnetic or electric field (that is, degeneracy is 1 for J=0 and 5 for J=2). The energy levels of an asymmetric top cannot be represented by an explicit formula like that of the spherical or symmetric top. Every level of the asymmetric top is characterized by a particular value of the quantum number J = 0,1,2,3,…For each value of J there are 2J+1 different energy levels, but the K quantum number is not defined as unique as in the symmetric top. Actually, the energy levels of the asymmetric top are somewhere between the limiting cases of the prolate symmetric and the oblate symmetric top and therefore can be obtained by smoothly connecting states of the same J in one limit to that of the same J in the other limit, without intersecting. That is why a basis set of symmetry adapted $|J, |K|, m\rangle$ functions are used, which is a linear combination of $|J, K, m\rangle$ and $|J, -K, m\rangle$. The even and odd values of K go with even and odd values of J resulting in rotational wavefunctions denoted as $|J, K_a, K_c, m\rangle$ where, the odd or even-ness of K_a and K_c associated with angular momentum about the a and c inertial axes (see Fig. 1) determine the symmetry species. So

K_a, K_c = even,even is A_1; K_a, K_c = odd,odd is A_2; K_a, K_c = odd,even is B_1; and K_a, K_c = even,odd is B_2. This also provides the answers to question 8.

6. The total wavefunction has to be antisymmetric (changes sign) with respect to interchange (permutation) of any two fermions and the total wavefunction has to be symmetric (not change sign) with respect to interchange of any two bosons. In H_2O the two protons are indistinguishable, therefore are interchanged by symmetry operations. In D_2O the two deuterons are likewise indistinguishable. Protons (spin ½) are fermions and deuterons (spin 1) are bosons. If we use α to denote the eigenfunction for $m=+\frac{1}{2}$ and β to denote $m=-\frac{1}{2}$, we can write down the eigenfunctions for the proton spin states. They are $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, $[\alpha(1)\beta(2)+\beta(1)\alpha(2)]/\sqrt{2}$, the eigenfunctions of both the z component of nuclear spin angular momentum and the square of said angular momentum; and also $[\alpha(1)\beta(2)-\beta(1)\alpha(2)]/\sqrt{2}$. Four altogether: the first three are symmetric (do not change sign) with respect to permutation of proton 1 with proton 2; the fourth one is antisymmetric (changes sign) with respect to permutation of proton 1 with proton 2. For the deuteron, if we use A to denote the eigenfunction for $m=+1$ and B to denote $m=-1$, Z to denote $m=0$, we can write down the eigenfunctions for the deuteron spin states. There are 9 altogether, the first six are symmetric with respect to permutation of deuteron 1 with deuteron 2: $A(1)A(2)$, $B(1)B(2)$, $Z(1)Z(2)$, $[A(1)B(2)+B(1)A(2)]/\sqrt{2}$, $[A(1)Z(2)+Z(1)A(2)]/\sqrt{2}$, $[Z(1)B(2)+B(1)Z(2)]/\sqrt{2}$, and the remaining three are antisymmetric (changes sign) with respect to permutation of 1 and 2: $[A(1)B(2)-B(1)A(2)]/\sqrt{2}$, $[A(1)Z(2)-Z(1)A(2)]/\sqrt{2}$, $[Z(1)B(2)-B(1)Z(2)]/\sqrt{2}$.

The nuclear spin statistical weights of 3 and 1 for H_2O (6 and 3 for D_2O) arise because in order to have the

TOTAL WAVEFUNCTION $\Psi = \psi_{\text{electronic}}\bullet\psi_{\text{vibrational}}\bullet\psi_{\text{rotational}}\bullet\psi_{\text{nuclearspin}}\bullet\psi_{\text{electron spin}}$ be antisymmetric with respect to interchange of proton 1 with proton 2 in H_2O, as dictated by Pauli exclusion principle, a particular rotational state can only go exclusively with particular nuclear spin states. The ground electronic state of water is of symmetry species totally symmetric, i.e. A_1, because it is a stable completely spin-paired system. (a product of an irreducible representation with itself, of a doubly occupied MO for example, always gives rise to a totally symmetric symmetry species). The rovibrational state $\psi_{\text{vibrational}}\bullet\psi_{\text{rotational}}$ is A_1 or B_1 or A_2 or B_2. Interchange of the protons leads to a change in sign of the rovibrational function in symmetry species B_1 or A_2 or B_2. Therefore these states can only have the $\psi_{\text{nuclearspin}}$ which are symmetric (three) for H_2O and antisymmetric (three) for D_2O, thereby resulting in TOTAL being antisymmetric for H_2O and symmetric for D_2O. At the same time the A_1 rovibrational states can have only the $\psi_{\text{nuclearspin}}$ which are antisymmetric (one) for H_2O and symmetric (six) for D_2O, thereby resulting in TOTAL being antisymmetric for H_2O and symmetric for D_2O.

7. Perturbation theory calculation of α involves terms of the type $\langle grd|\mu|exc\rangle\langle exc|\mu|grd\rangle/E_{exc}\text{-}E_{grd}$, where the dipole moment operator μ_x or μ_y or μ_z can be in each of the integrals. Since μ_x is a sum of charge times x Cartesian coordinate, μ_x transforms as the x coordinate itself. Thus the components of α transform as the product of Cartesians. To find the symmetry species of the products of Cartesians we can take products of the irreducible representations (as found in question 1) of the Cartesian coordinates x,y,z. $A_1xA_1 = A_1$, $B_1xB_1=A_1$, $B_2xB_2=A_1$, $B_1xB_2=A_2$, $A_1xB_1=B_1$, $A_1xB_2=B_2$.

C_{2v}		
A_1	x	xx,yy,zz
A_2	R_x	yz
B_1	z, R_y	xz
B_2	y, R_z	xy

8. Now we can use the above to complete TABLE 2. First the answers to question 5 permit us to fill in the first column. Then the answers to question 7 permit us to fill in each row of the second column.

Symmetry species	Components of the polarizability tensor	Rotational selection rules in K_a and K_c use these!		Allowed transitions (You do not need to know what is below in this column; given just for completeness)
		ΔK_a	ΔK_c	
B_1	α_{xz}	odd	even	ee↔oe, eo↔oo
A_2	α_{yz}	odd	odd	ee↔oo, eo↔oe
A_1	$\alpha_{xx},\alpha_{yy},\alpha_{zz}$	even	even	ee↔ee,oo↔oo,eo↔eo,oe↔oe
B_2	α_{xy}	even	odd	ee↔eo, oe↔oo

9. The intensity of a Raman line is proportional to

$$(\pi/\varepsilon_0)^2 \bullet (\nu_0-\nu)^4 \bullet w_i \bullet \exp[-E_i/k_BT]/Z(T) \bullet |\langle f \mid \alpha_{MN} \mid i\rangle|^2.$$

The intensity of a spectral line is determined, in general, by
the probability that a molecule is in the initial energy level
times
the probability per unit time that a given molecule will undergo a transition from the initial state i to the final state f due to the effect of the perturbing electromagnetic radiation.

$(\nu_0-\nu)^4$ arises because Raman is a light scattering process and the intensity of scattered light is in general proportional to frequency of the light to the fourth power.

$w_i \bullet \exp[-E_i/k_BT]/Z(T)$ is the fractional population of the level with energy E_i, the initial energy level, according to statistical mechanics, since (for corrected boltzons) the probability of finding any one molecule in level E_i (N_i/N) is $N_i/N = g_i\exp[-E_i/k_BT]/Z(T)$, where Z(T) is the partition function. For the initial level of H_2O, the total degeneracy g_i is given by the number of nuclear spin states, 1 or 3, times the number of rotational m states, 2J+1 (This is part of the answer to question 10). w_i is the number of nuclear spin states that is permitted by the

Pauli exclusion principle, as explained in the answer to question 6. The population of an energy level is proportional to the number of different states have the same energy.

The probability per unit time that a given molecule will undergo a transition from the initial state i to the final state f due to the effect of the perturbing electromagnetic radiation is given by

$2\pi/3\hbar^2 \bullet$(total radiation energy per unit volume per unit frequency) $\bullet |\langle f | \mu_M | i \rangle|^2$ when it is an electric dipole transition involving the electric field of the radiation. We replace $|\langle f | \mu_M | i \rangle|^2$ by $|\langle f | \alpha_{MN} | i \rangle|^2$ because the induced electric dipole moment rather than the electric dipole moment is involved in Raman scattering, $|\langle f | \alpha_{MN} | i \rangle|^2$ is the square of the transition moment integral.

10. In a single crystal where M and N are the components of Cartesian space-fixed axes, each molecule has a fixed orientation with respect to the space-fixed axes. In a gas, molecules can isotropically orient individually. Therefore averaging over all orientations is required. Furthermore the above expression has to be added up over all values of the magnetic quantum number (see answer to question 9: degeneracy g_i must include 2J+1), since the energy is independent of $m=0, \pm 1, \pm 2, \pm 3, \ldots \pm J$.

Examples of *V* for the H_2O molecule are given in the answer to question 4. 000, 110, 001, etc.

11. The definition of the molecular partition function Z(T) is, from statistical mechanics, $Z(T) = \sum_i g_i \exp[-E_i/k_B T]$, where g_i is the degeneracy of state i as given in the answer to question 9, and E_i is the energy of state i for the molecule such as H_2O, including electronic, vibrational, rotational, nuclear spin, electron spin.

12. This is just like the expansion of V in the answer to question 4, in terms of the powers of the symmetry coordinates S_1^2, S_1S^2, S_2^2, etc. Every term in the expansion has to be the same symmetry specie as V, that is, totally symmetric, because the value of V can not change sign when someone changes the orientation of the axes (which is the equivalent of carrying out symmetry operations such as reflection, inversion). In the same way, in the expansion of the α_{xz} for example in terms of the dimensionless normal coordinates of the molecule,

$$\alpha_{xz} = \alpha_{xz\,\mathrm{equil}} + \sum_j (\partial\alpha_{xz}/\partial q_j)_{\mathrm{equil}}\, q_j + \ldots$$

every term in the expansion has to belong to the same symmetry species as α_{xz}. Therefore, since α_{xz} belongs to the symmetry species B_1 (as seen in the answer to question 7), then the only q_j that can exist in the expansion is the normal coordinate that belongs to B_1, that is, q_3. (See Fig. 1 for this coordinate.) This means that the derivative $(\partial\alpha_{xz}/\partial q_j)_{\mathrm{equil}}$ must vanish for q_1 and q_2. Similarly for the xx component, only the derivative $(\partial\alpha_{xx}/\partial q_1)_{\mathrm{equil}}$ is not zero. The vibrational Raman intensity depends on these derivatives.

13. In the harmonic approximation, only the q_i terms in the expansion are needed, the only non-vanishing $\langle V' | \alpha | V \rangle$ by symmetry are:

$\langle 100 | \alpha | 000 \rangle = [(\partial\alpha_{xx}/\partial q_1)_{\mathrm{equil}} + (\partial\alpha_{yy}/\partial q_1)_{\mathrm{equil}} + (\partial\alpha_{zz}/\partial q_1)_{\mathrm{equil}}] \langle 100 | q_1 | 000 \rangle$

$\langle 001 | \alpha | 000 \rangle = (\partial\alpha_{xz}/\partial q_3)_{\mathrm{equil}} \langle 001 | q_3 | 000 \rangle$

14. There are only the four transitions observed because at 3 K there is no population in the energy levels other than the lowest ones due to the unfavorable exp[-E_i/k_BT]. The zero-point vibrational state $|000\rangle$ has all of the population, of course, and same goes for rotation. This means that all transitions that are observed at 3 K begin from $|000\rangle|J=0,K_a=0,K_c=0\rangle$. Raman selection rule for J is $\Delta J = 0,\pm2$. From the answer to question 13, we see that it is possible to observe these two scattering lines at the frequencies corresponding to ν_1 and ν_3, which, in the harmonic approximation correspond to the energy differences between $|100\rangle$ and $|000\rangle$, between $|001\rangle$ and $|000\rangle$, respectively. Accompanying the vibrational excitation from $|000\rangle$ to $|100\rangle$ are the $J=0\rightarrow J=0$ transition (Q branch), and the $J=0\rightarrow J=2$ transition (the S branch). There are two of these $K_a=0,K_c=0$, $J=0$ to either $K_a=2$ $K_c=0$ or to $K_a=0$ $K_c=2$ (only even-even go with A_1 vibrations as seen in question 8). Accompanying the vibrational excitation from $|000\rangle$ to the B_1 vibrational state $|001\rangle$ is the $J = 0,K_a=0,K_c=0$, transition to $J = 2$, $K_a=1,K_c=2$, (only odd-even go with B_1 vibrations as seen in question 8).