Chemistry 416, Dr. Glaser

Applications of IR/Raman Spectra: Hydrogenfluoride Hydrate

Attached you will find (parts of) the printout of an *ab initio* calculation a hydrogen-bonded supersystem between H_20 and HF. The calculation was carried out at the RHF/3-21G level, the same level we used in the calculation of water in the previous assignment.

(a) Make a drawing of the molecule using the Cartesian coordinates found in the section "Standard Orientation".

(b) Draw the normal mode representations as described in the previous assignment.

(c) Considering your drawings of the normal modes, name these vibrations as "stretching" and "bending" modes and so on and state whether they are "symmetric" or "asymmetric".

(d) Now let's consider the number of frequencies. Calculate the number of vibrations. How many frequencies are we observing? How does this compare to free water and free HF? Explain the discrepancy (if any).

(e) Compare and contrast the vibrational frequencies of the small H-bonded "cluster" to the vibrational frequencies of free water and free hydrogenfluoride.

(f) Compare and contrast the IR and Raman intensities of the vibrations of the small H-bonded "cluster" to the vibrational frequencies of free water and free hydrogenfluoride.

(2 attachments, freq. calc. of H-bonded cluster H_20---HF and of HF at RHF/3-21G).

HF RHF/3-21G freq

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STOICHIOMETRY    FH
FRAMEWORK GROUP  C*V[C*(HF)]
DEG. OF FREEDOM    1
FULL POINT GROUP                 C*V     NOP  4
LARGEST ABELIAN SUBGROUP         C2V     NOP  4
LARGEST CONCISE ABELIAN SUBGROUP C1      NOP  1
                  Standard orientation:
---------------------------------------------------------------
Center     Atomic              Coordinates (Angstroms)
Number     Number             X           Y           Z
---------------------------------------------------------------
   1          9           0.000000    0.000000    0.093746
   2          1           0.000000    0.000000   -0.843711
---------------------------------------------------------------
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
Raman scattering activities (A**4/AMU), Raman depolarization ratios,
reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                     1
                    SG
Frequencies --  4061.1820
Red. masses --     1.0583
Frc consts  --    10.2841
IR Inten    --    32.9441
Raman Activ --    42.1138
Depolar     --     0.3825
Atom AN      X      Y      Z
  1   9     0.00   0.00   0.05
  2   1     0.00   0.00  -1.00
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HF--h2o freq RHF/3-21G

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 STOICHIOMETRY    FH3O
 FRAMEWORK GROUP  C2V[C2(OHF),SGV(H2)]
 DEG. OF FREEDOM    4
 FULL POINT GROUP                 C2V     NOP  4
 LARGEST ABELIAN SUBGROUP         C2V     NOP  4
 LARGEST CONCISE ABELIAN SUBGROUP C2      NOP  2
                   Standard orientation:
 ---------------------------------------------------------------
 Center     Atomic              Coordinates (Angstroms)
 Number     Number             X           Y           Z
 ---------------------------------------------------------------
    1          8           0.000000    0.000000   -1.181951
    2          1           0.000000    0.000000    0.433047
    3          9           0.000000    0.000000    1.386971
    4          1           0.000000    0.792814   -1.730090
    5          1           0.000000   -0.792814   -1.730090
 ---------------------------------------------------------------
0Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                     1                      2                      3
                    B1                     B2                     A1
 Frequencies --    34.4199               247.1024               317.0515
 Red. masses --     1.1751                 1.0971                 7.0251
 Frc consts  --     0.0008                 0.0395                 0.4161
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IR Inten	--	388.9275			25.5626			5.2588			
Raman Activ	--	4.8694			3.4371			0.0837			
Depolar	--	0.7500			0.7500			0.2588			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z	
1	8	-0.10	0.00	0.00	0.00	0.07	0.00	0.00	0.00	-0.45	
2	1	-0.14	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.41	
3	9	0.02	0.00	0.00	0.00	-0.04	0.00	0.00	0.00	0.41	
4	1	0.70	0.00	0.00	0.00	-0.33	-0.57	0.00	-0.02	-0.48	
5	1	0.70	0.00	0.00	0.00	-0.33	0.57	0.00	0.02	-0.48	
		4			5			6			
		B1			B2			A1			
Frequencies	--	820.8076			999.1024			1780.8252			
Red. masses	--	1.0427			1.0470			1.0985			
Frc consts	--	0.4139			0.6157			2.0526			
IR Inten	--	358.7625			290.0801			86.0628			
Raman Activ	--	3.6472			1.2070			8.5031			
Depolar	--	0.7500			0.7500			0.4735			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z	
1	8	0.03	0.00	0.00	0.00	-0.04	0.00	0.00	0.00	-0.08	
2	1	-0.99	0.00	0.00	0.00	0.95	0.00	0.00	0.00	-0.02	
3	9	0.03	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	0.00	
4	1	-0.07	0.00	0.00	0.00	0.10	0.20	0.00	0.39	0.59	
5	1	-0.07	0.00	0.00	0.00	0.10	-0.20	0.00	-0.39	0.59	
		7			8			9			
		A1			A1			B2			
Frequencies	--	3712.2279			3867.7530			4001.8236			
Red. masses	--	1.0583			1.0387			1.0874			
Frc consts	--	8.5924			9.1551			10.2606			
IR Inten	--	745.7964			12.2682			82.2426			
Raman Activ	--	51.8499			87.1267			45.3345			
Depolar	--	0.4123			0.1804			0.7500			
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z	
1	8	0.00	0.00	0.00	0.00	0.00	-0.05	0.00	0.07	0.00	
2	1	0.00	0.00	1.00	0.00	0.00	-0.02	0.00	0.00	0.00	
3	9	0.00	0.00	-0.05	0.00	0.00	0.00	0.00	0.00	0.00	
4	1	0.00	0.00	0.02	0.00	-0.61	0.36	0.00	-0.58	0.40	
5	1	0.00	0.00	0.02	0.00	0.61	0.36	0.00	-0.58	-0.40	