Chemistry 416 "Spectroscopy"
Fall Semester 1993
Dr. Rainer Glaser

Second 1-Hour Examination
"IR/Raman Spectroscopy"

Monday, October 4, 1993, 8:40 - 9:30

Name:

| Question 1	35	
Question 2	40	
Question 3	25	
Total		

Question 1. Interpretation of IR and Raman Spectra. (35 points)

Mostly taken from the required texts and the assignments. As always, it pays to study and to do the homework! Five parts to this question.

(a) The spectrum is shown of an aromatic toluene derivative with the formula C_8H_7N. Give the structural formula of this compound and, in particular, indicate the bands based on which you assign the correct substitution pattern. (5 points)
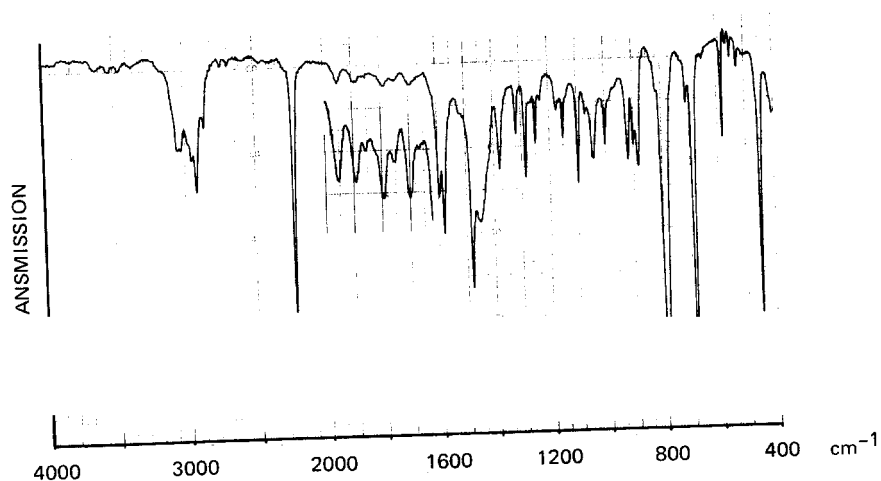
(b) The spectra are shown of $C_5H_{11}COOCH_3$, C_4H_9-O-C_4H_9 and C_4H_6-CEt-CH_2OH (not necessarily in this order!). Indicate which spectrum corresponds to which compound. Clearly indicate all the bands on which you base your assignment and state what types of modes they are (stretch, bend, and so on). When appropriate, state whether the peaks correspond to "symmetric" or "antisymmetric" modes. Write on spectra. (12 points)
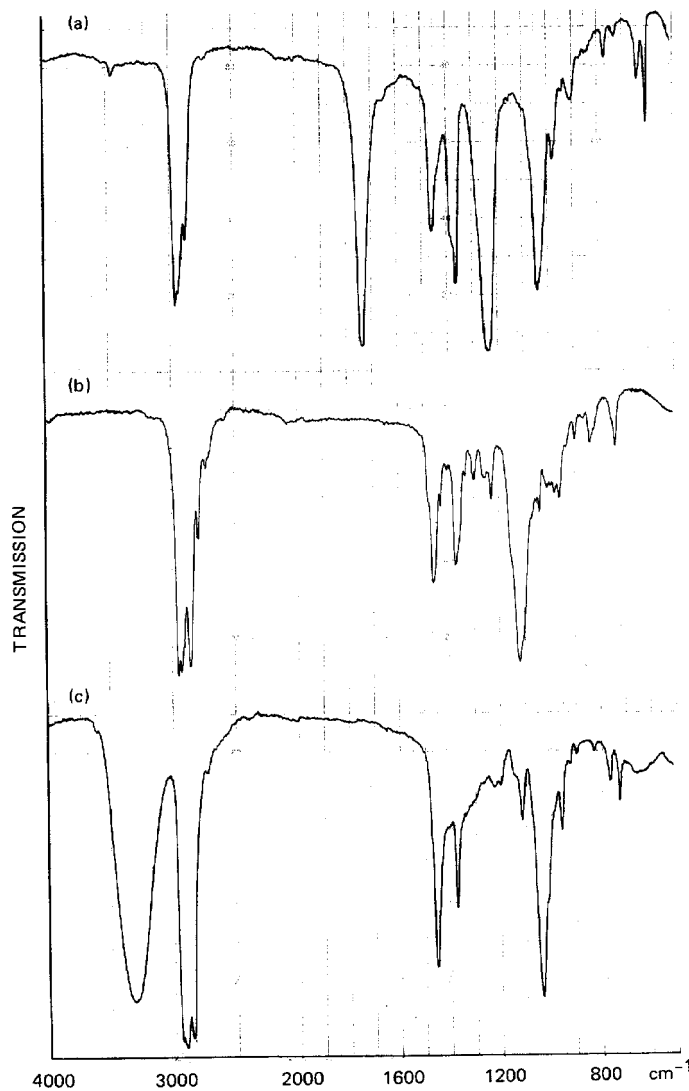
(c) The IR and Raman spectra are shown of a compound with formula $C_6H_5NO_2$. Indicate which spectrum is the IR and which is the Raman spectrum. Indicate the significant peaks and state what types of normal modes they represent. Briefly explain your assignments. (8 points)

(a)

(b)

3500   3000   2500   2000   1600   1200   800   400   cm^{-1}
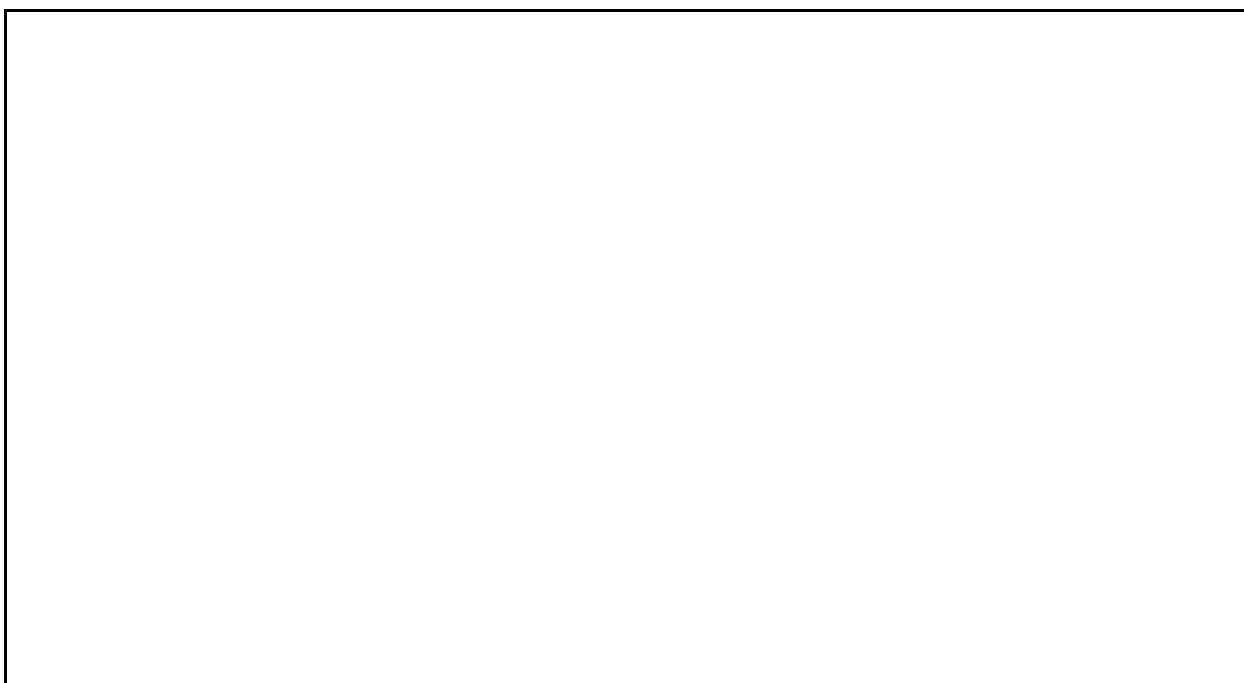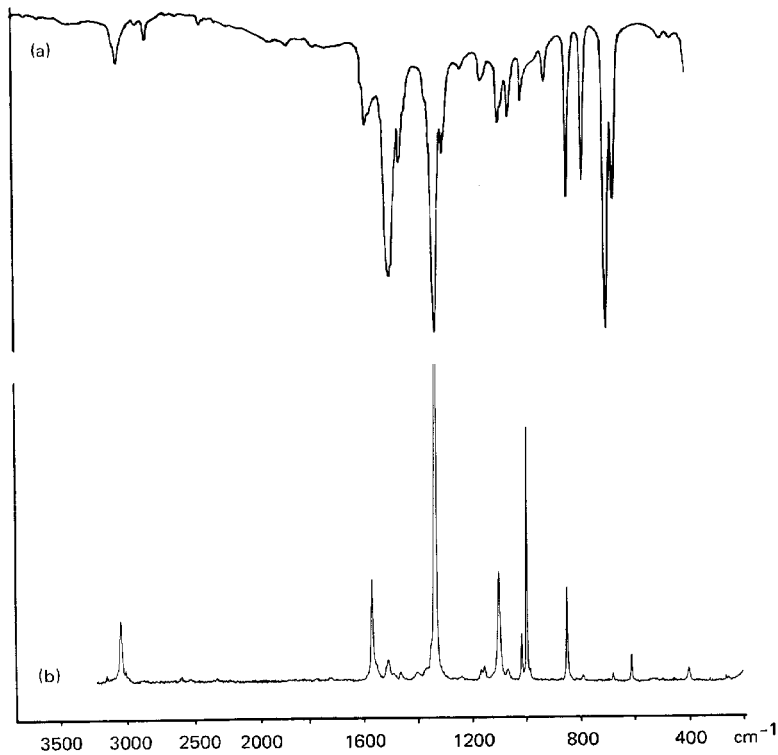
(d) The IR spectrum of an unknown is shown. The unknown contains only C, O and H, it is high-boiling (206 °C), and its molecular weight is 138. What is it? Argue briefly. (10 points)
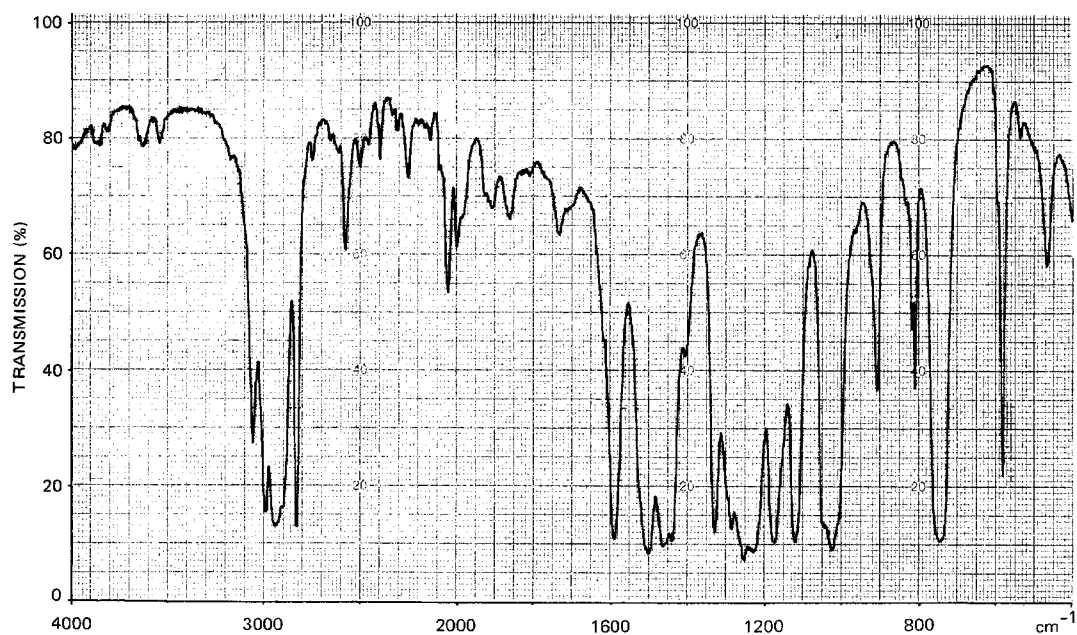
Argue:

Question 2. Normal Mode Analysis.

Let's consider the IR and Raman spectra of **O=C=O**, **S=C=S**, and **O=C=S**. For each system, the results of *ab initio* calculations (RHF/6-31G*) for the linear structures are summarized below. You will find the Cartesian coordinates and the vibrational information below. (You are familiar with the format because of previous assignments associated with Chemistry 416.)

O=C=O

```
STOICHIOMETRY      CO2
FRAMEWORK GROUP   D*H[O(C),C*(O.O)]
DEG. OF FREEDOM    1
FULL POINT GROUP                    D*H      NOP  8
LARGEST ABELIAN SUBGROUP            D2H      NOP  8
LARGEST CONCISE ABELIAN SUBGROUP C2          NOP  2
                   Standard orientation:
-----------------------------------------------------------
Center      Atomic                Coordinates (Angstroms)
Number      Number              X           Y           Z
-----------------------------------------------------------
   1          8          0.000000    0.000000    1.143272
   2          6          0.000000    0.000000    0.000000
   3          8          0.000000    0.000000   -1.143272
-----------------------------------------------------------
```
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			2			3		
				PIU			PIU			SGG	
Frequencies --				745.8556			745.8556			1518.4149	
Red. masses --				12.8774			12.8774			15.9949	
Frc consts --				4.2207			4.2207			21.7277	
IR Inten --				68.9315			68.9315			0.0000	
Raman Activ --				0.0000			0.0000			12.3315	
Depolar --				0.0000			0.0000			0.1938	
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 8	0.33	0.00	0.00	0.00	0.33	0.00	0.00	0.00	-0.71
2 6	-0.88	0.00	0.00	0.00	-0.88	0.00	0.00	0.00	0.00
3 8	0.33	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.71

		4		
		SGU		
Frequencies --	2584.8705			
Red. masses --	12.8774			
Frc consts --	50.6938			
IR Inten --	988.5750			
Raman Activ --	0.0000			
Depolar --	0.0000			
Atom AN	X	Y	Z	
1 8	0.00	0.00	-0.33	
2 6	0.00	0.00	0.88	
3 8	0.00	0.00	-0.33	

S=C=S

```
STOICHIOMETRY      CS2
FRAMEWORK GROUP   D*H[O(C),C*(S.S)]
DEG. OF FREEDOM    1
FULL POINT GROUP                      D*H     NOP  8
LARGEST ABELIAN SUBGROUP              D2H     NOP  8
LARGEST CONCISE ABELIAN SUBGROUP C2          NOP  2
                     Standard orientation:
---------------------------------------------------------
Center      Atomic            Coordinates (Angstroms)
Number      Number          X           Y           Z
---------------------------------------------------------
   1          16         0.000000    0.000000    1.544565
   2           6         0.000000    0.000000    0.000000
   3          16         0.000000    0.000000   -1.544565
---------------------------------------------------------
```

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                      2                      3
                     PIU                    PIU                    SGG
Frequencies --    445.4418               445.4418               724.9964
Red. masses --     13.3142                13.3142                31.9721
Frc consts  --      1.5565                 1.5565                 9.9013
IR Inten    --      0.0037                 0.0037                 0.0000
Raman Activ --      0.0000                 0.0000                19.3739
Depolar     --      0.0000                 0.0000                 0.2604
Atom AN      X      Y      Z       X      Y      Z       X      Y      Z
  1  16    0.00   0.18   0.00    0.18   0.00   0.00    0.00   0.00  -0.71
  2   6    0.00  -0.97   0.00   -0.97   0.00   0.00    0.00   0.00   0.00
  3  16    0.00   0.18   0.00    0.18   0.00   0.00    0.00   0.00   0.71
                      4
                     SGU
Frequencies --   1583.0430
Red. masses --     13.3142
Frc consts  --     19.6585
IR Inten    --   1505.4966
Raman Activ --      0.0000
Depolar     --      0.0000
Atom AN      X      Y      Z
  1  16    0.00   0.00  -0.18
  2   6    0.00   0.00   0.97
  3  16    0.00   0.00  -0.18
```

O=C=S
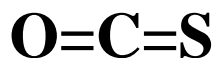
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STOICHIOMETRY     COS
FRAMEWORK GROUP   C*V[C*(OCS)]
DEG. OF FREEDOM    2
FULL POINT GROUP                      C*V    NOP  4
LARGEST ABELIAN SUBGROUP              C2V    NOP  4
LARGEST CONCISE ABELIAN SUBGROUP C1   NOP  1
                  Standard orientation:
-----------------------------------------------------------
Center    Atomic              Coordinates (Angstroms)
Number    Number          X            Y            Z
-----------------------------------------------------------
   1        8          0.000000     0.000000    -1.668196
   2        6          0.000000     0.000000    -0.536871
   3       16          0.000000     0.000000     1.035425
-----------------------------------------------------------

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                      2                      3
                   PI                     PI                     SG
Frequencies --   566.5350               566.5350               889.0429
Red. masses --    13.0313                13.0313                19.4168
Frc consts  --     2.4643                 2.4643                 9.0422
IR Inten    --    19.7658                19.7658                46.7736
Raman Activ --     1.2681                 1.2681                 7.9680
Depolar     --     0.7500                 0.7500                 0.1932
Atom AN     X       Y      Z       X       Y      Z       X       Y      Z
  1   8   0.00    0.40   0.00    0.40    0.00   0.00    0.00    0.00  -0.67
  2   6   0.00   -0.91   0.00   -0.91    0.00   0.00    0.00    0.00  -0.52
  3  16   0.00    0.14   0.00    0.14    0.00   0.00    0.00    0.00   0.53
                   4
                   SG
Frequencies --  2305.9773
Red. masses --    13.2273
Frc consts  --    41.4412
IR Inten    --  1181.3391
Raman Activ --    27.9237
Depolar     --     0.3758
Atom AN     X       Y      Z
  1   8   0.00    0.00  -0.55
  2   6   0.00    0.00   0.84
  3  16   0.00    0.00  -0.04
```

(a) The total number of degrees of freedom for each of these linear molecules is _____. This number results from the formula _____ where N denotes the number of atoms. Of the total number of degrees of freedom, a total of _____ are not vibrations but rather there are ____ degrees of freedom for translation and ____ degrees of freedom for _____. (6 p)

(b) Let's consider the stretching modes of two of these molecules. Identify all the stretching modes for each molecule. For each stretching mode, draw the molecule and use vectors to indicate the motion of each atom in the molecule. Write down whether the mode is *symmetric* or *asymmetric* in each case. (12 p)

O=C=O

O=C=S
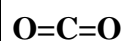
(c) Let's compare the IR and Raman activities of these three molecules. (10 points)

As you can see, for O=C=O and S=C=S, only one of the stretching frequencies is IR active. Which one is it? Explain why one stretching mode is active while the other one is not.

Briefly explain why only one of the stretching modes of O=C=O and S=C=S is active in Raman active. Compare the situation to the IR-activity.

Briefly explain why both stretching modes in O=C=S are both IR and Raman active.

(d) Group vibrations can be computed fairly well based on the force constants and the reduced mass of the vibrating system. At the very least, the respective formula is very useful to make qualitative decisions when shifts of bands are being considered. Let's try that by considering some labeled compounds. Remember that the potential energy surface does not depend on the atomic masses, that is, the force constants remain the same. (12 points)

What is the effect on the *symmetric stretching frequency* caused by the replacement of both ^{16}O by ^{17}O in $O=C=O$? Briefly explain.

What is the effect on the *symmetric stretching frequency* caused by the replacement of ^{12}C by ^{13}C in $O=C=O$? Briefly explain.

What is the effect on the *asymmetric stretching frequency* caused by the replacement of ^{12}C by ^{13}C in $O=C=O$? Briefly explain.

Question 3. Solvent Effects on the IR Spectra of Nitro-*N*-methylaniline.

Gonzalez, G.; Clavijo, E. *J. Chem. Soc. Perkin Trans II* **1985**, 1751-1754.

(a) In Table 1, the N-H stretching frequencies are listed for various solvents. What happens to the N-H stretching frequency of *N*-methylaniline as the polarity of the solvent increases? Explain this shift by considering the solvent effects on the N-H force constant. (5 p)

Table 1. Solvent effects on the N–H stretching frequency in *N*-methylaniline and its nitro derivatives

Solvent	DN^a	*N*-Methylaniline v(N–H)	Δv(CCl$_4$)	*para*-Nitro-*N*-methylaniline v(N–H)	Δv(CCl$_4$)	*ortho*-Nitro-*N*-methylaniline v(N–H)	Δv(CCl$_4$)
Carbon tetrachloride (CCl$_4$)		3 457	0	3 464	0	3 410	0
Benzene (BZ)	0.1	3 445	12	3 435	29	3 411	−1
Nitromethane (NM)	2.7			3 437	27	3 412	−2
Nitrobenzene (NB)	4.4	3 428	29	3 427	37	3 409	1
Acetonitrile (AN)	14.1	3 420	37	3 409	55	3 404	6
Dioxane (DX)	14.8	3 417	40	3 390	74	3 405	5
Propane-1,2-diol carbonate (PDC)	15.1	3 425	32	3 400	64	3 409	1
Acetone (AC)	17.0	3 409	48	3 390	74	3 399	11
Diethyl ether (Et$_2$O)	19.2	3 399	58	3 363	101	3 405 / 3 384	5 / 26
Tetrahydrofuran (THF)	20.0	3 396	61	3 348	116	3 408 / 3 380	2 / 30
Trimethyl phosphate (TMP)	23.0	3 380	77	3 325	139	3 408 / 3 375	2 / 35
N,*N*-Dimethylacetamide (DMA)	27.8			3 295	169	3 406 / 3 360	4 / 50
Dimethyl sulphoxide (DMSO)	29.8	3 342	115	3 286	178	3 407 / 3 355	3 / 55
Pyridine (PY)	33.0	3 326	131	3 270	194	3 405 / 3 345	5 / 65

^{a} Solvent donor numbers from ref. 16.

(b) The N-H stretching information from Table 1 is shown graphically (and more complete) in Figure 1. Note in particular that there are two peaks for the N-H stretch of the *ortho*-nitro-*N*-methylaniline. Draw the structures of the two isomers that cause these two peaks. Assign each peak to the correct isomer and explain your reasoning. (12 p)
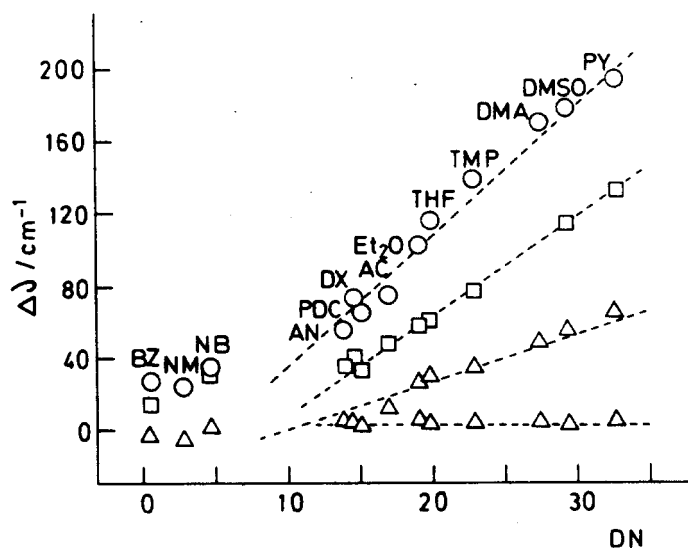

Figure 1. Influence of the medium donor strength on the N–H frequency shifts, $\Delta v(CCl_4)$, for *ortho*-nitro-*N*-methylaniline ($\triangle$), *para*-nitro-*N*-methylaniline ($\bigcirc$), and *N*-methylaniline ($\square$).

(c) For a given solvent, the N-H stretching frequency of the *ortho* isomer is shifted much less than that of the *para*-isomer. The unsubstituted system is shifted by a value in-between the substituted systems. Explain why the shift is more for the *para* isomer than for the parent system. Explain why the shift is less for the *ortho* isomer compared to the parent system. (8)

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para:

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ortho: