Chemistry 416 "Spectroscopy"
Fall Semester 1997
Dr. Rainer Glaser
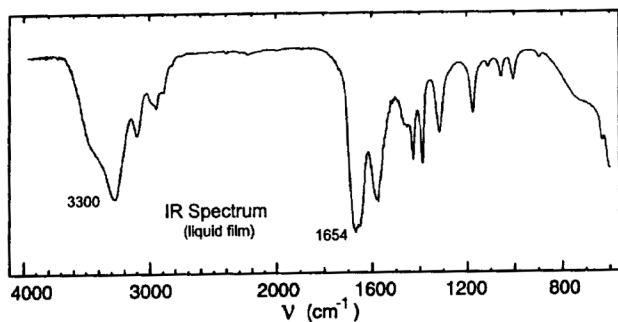
Third 1-Hour Examination
"Vibrational Spectroscopy"

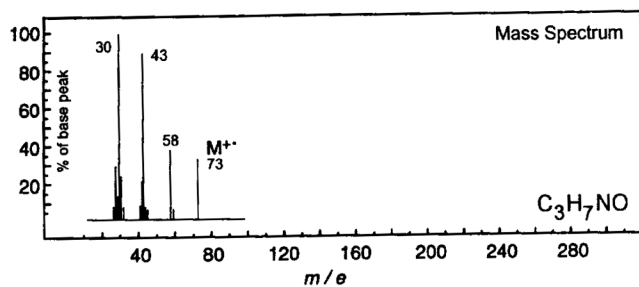### Monday, November 24, 1997, 8:40 - 9:30

Name:

Question 1 (Combination)	25	
Question 2 (Environment)	14	
Question 3 (Hydrocarbons)	11	
Question 4 (Functionality)	10	
Question 5 (Normal Modes)	40	
Total	100	

Question 1. Combination Problem. (25 points)

problem 60

IR Spectrum (liquid film) — 3300, 1654

Mass Spectrum — 30, 43, 58, M+· 73

C_3H_7NO

No significant UV absorption above 220 nm

13C NMR Spectrum (50.0 MHz, CDCl₃ solution)

DEPT CH₂↓ CH₃↑ CH↑

solvent

proton decoupled

1H NMR Spectrum (200 MHz, CDCl₃ solution)

expansion with irradiation (decoupling) at δ 7.4 ppm

expansion

exchanges with D₂O on warming

TMS
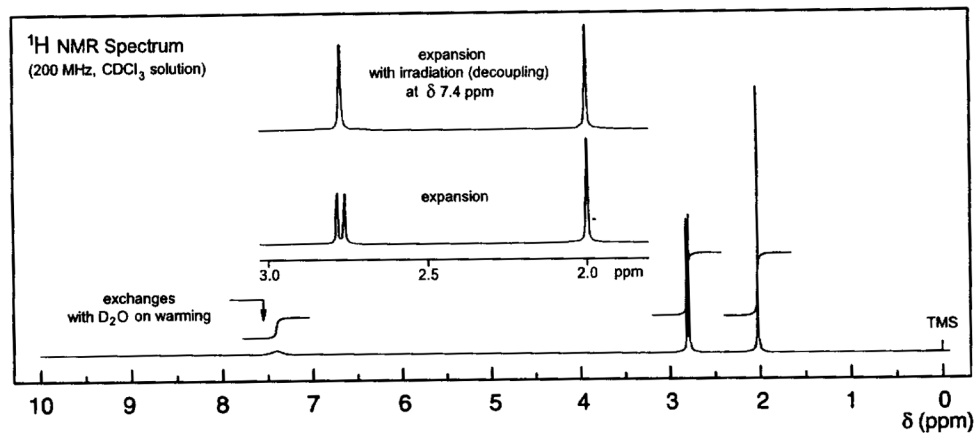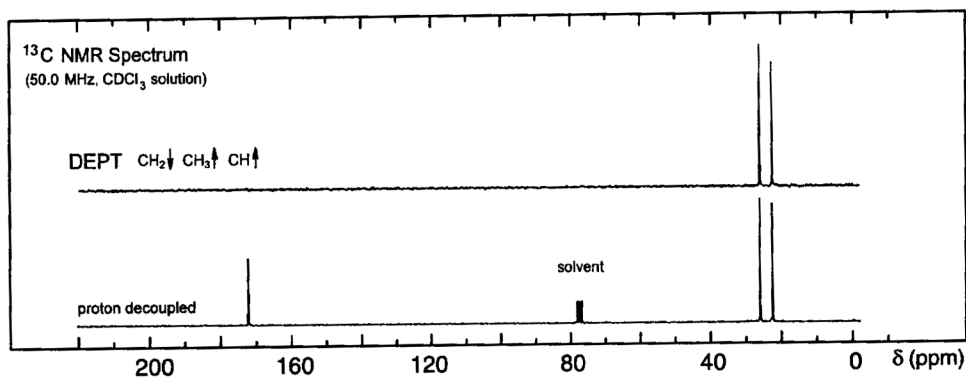
(a) Draw the **structure** and give the correct **name** of the unknown. (9 points)

(b) Name all of the types of **stretching modes** that contribute to the spectrum above 2,800 1/cm. (6 p.)

(c) Which band(s) in the **fingerprint region** is / are characteristic for the functional group type present. Identify this band / these bands in the spectrum and give its / their wave number(s) and state what functionality they are indicative of. (5 points)

(d) Suppose the spectrum of the unknown were recorded in the **vapour phase**. What would be the one most significant difference in the spectrum. (5 points)

Question 2. Recording of IR Spectra and Effect on Spectra. (14 points)
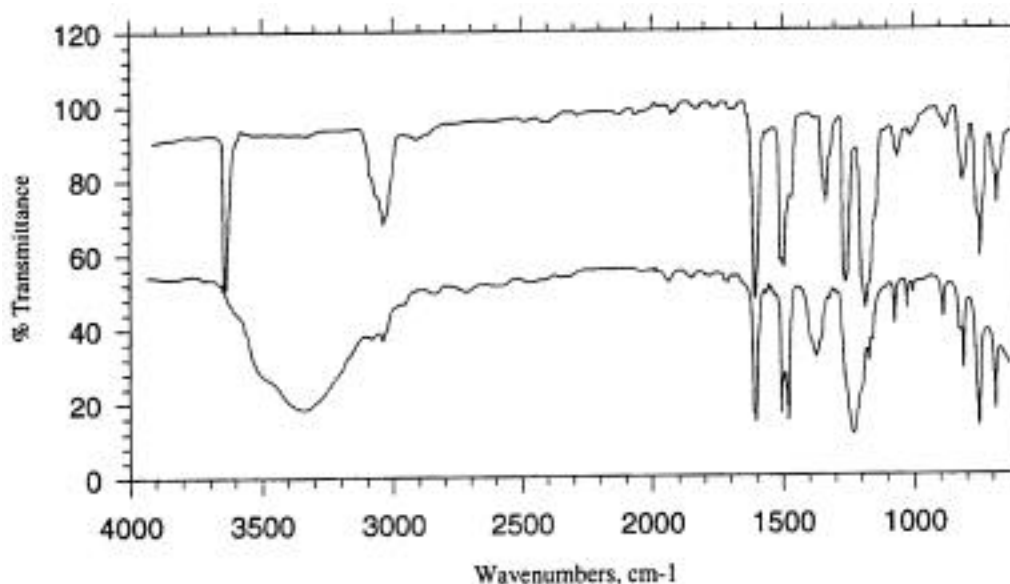
The IR spectra are shown of **phenol**. One of the spectra was recorded fort a **liquid film** of phenol and the other spectrum is the **vapour phase** spectrum.

(a) Indicate in the picture above which spectrum was recorded in the vapour phase and which one was recorded for the liquid film. (4 points)

(b) Describe the major differences between the spectra. State what band is affected (position and shape) the most and explain why this band is affected in this way. Use structural drawings to indicate the intermolecular interactions responsible for these effects. (10 points)

Question 3. Hydrocarbon Spectrum. (11 points)
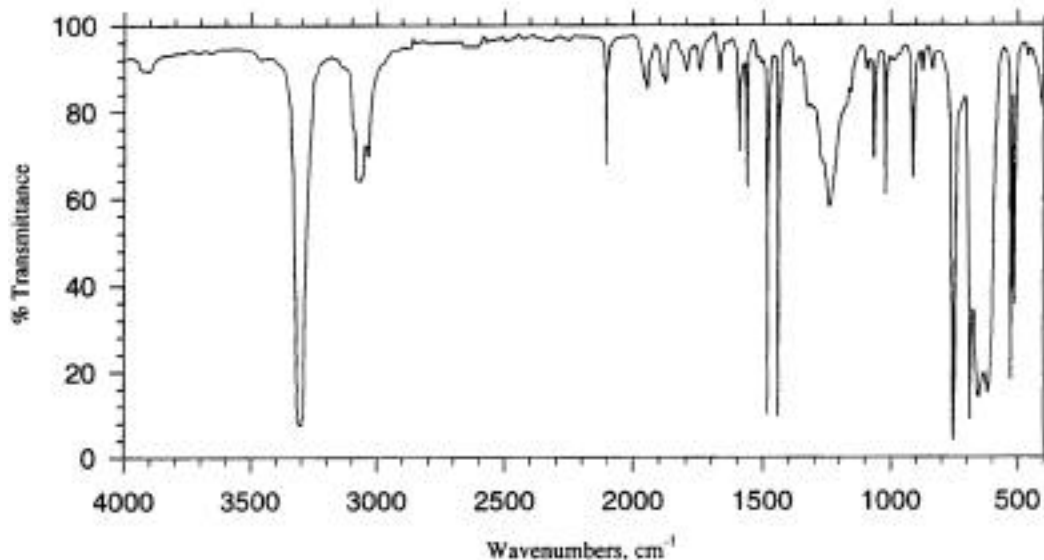
(a) The IR spectrum is shown of **phenylacetylene**. Draw the structure of this compound. (2 points)
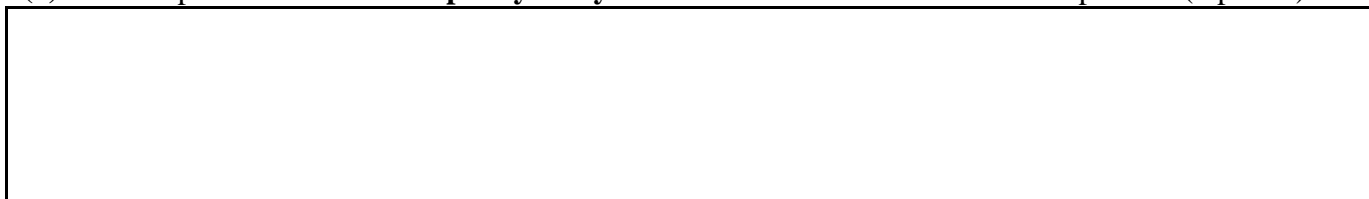
(b) Assign all bands that occur above 2,500 1/cm. Clearly state what types of normal modes these bands are associated with. Explain the **effect of the C-hybridization** on the vibrational frequency. (6 p)
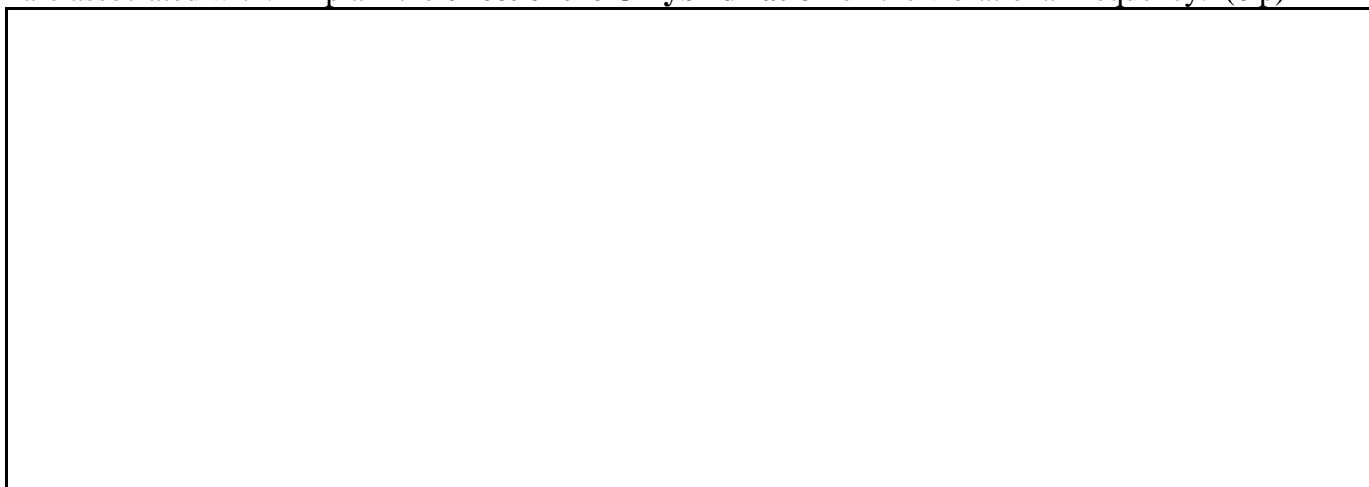
(c) In the above spectrum, indicate the peak that corresponds to the **carbon-carbon triple bond stretching mode** and write down at what wave number this band occurs in this case. (3 points)

Question 4. Functional Group Recognition. (10 points)

% Transmittance vs. Wavenumber, cm^{-1} (IR spectrum, axes 4000–500 cm^{-1}, 0–120 % Transmittance)
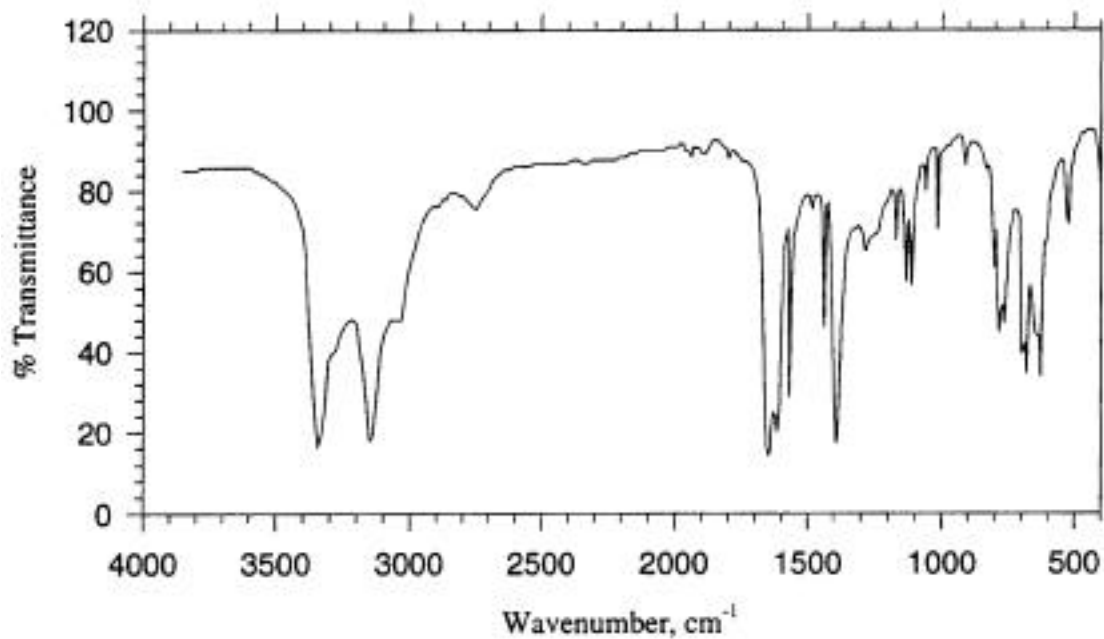
(a) Analyze the IR spectrum shown and determine what type of compound is consistent with this spectrum.   You do not need to provide the structure of the actual compound for which this spectrum was recorded. Rather, it is the goal to recognize the functional group. You do need to argue which bands are characteristic for that functional group.

Question 5. Normal Mode Analysis. (40 points)

We will be looking at the normal mode analysis of **formamide**. An ab initio computation of the compound has been carried out and the printout is attached below (after some editing).

$$
\begin{array}{c}
\text{H} \\
\quad \diagdown \\
\qquad \text{C}\!=\!\text{O} \\
\quad \diagup \\
\text{H}\!-\!\text{N} \\
\qquad \diagdown \\
\qquad \text{H}
\end{array}
$$
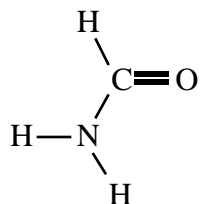
(a) The Amino Inversion.

Draw the displacement vector of the normal mode with the lowest vibrational frequency in the space below. (5 points)

y

x
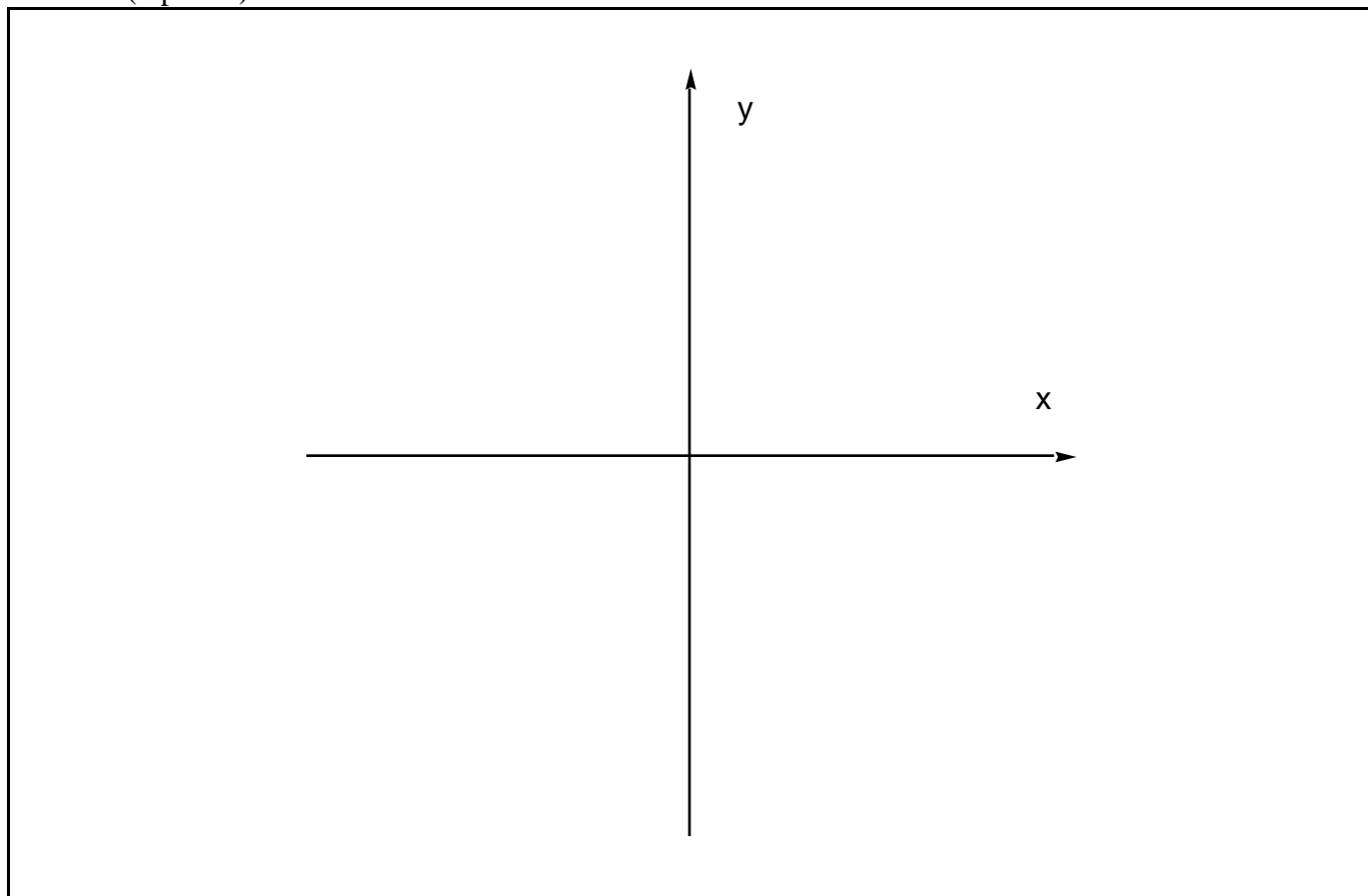
(b) The "CO Stretch". (15 points)

Via inspection of the computed normal modes, identify that mode that corresponds mostly to the CO stretching mode of formamide. The band is computed to occur at _____ 1/cm. (5 points)

Draw the displacement vector of this normal mode (and note that it is not a pure CO stretch). (5 p.)

y

x
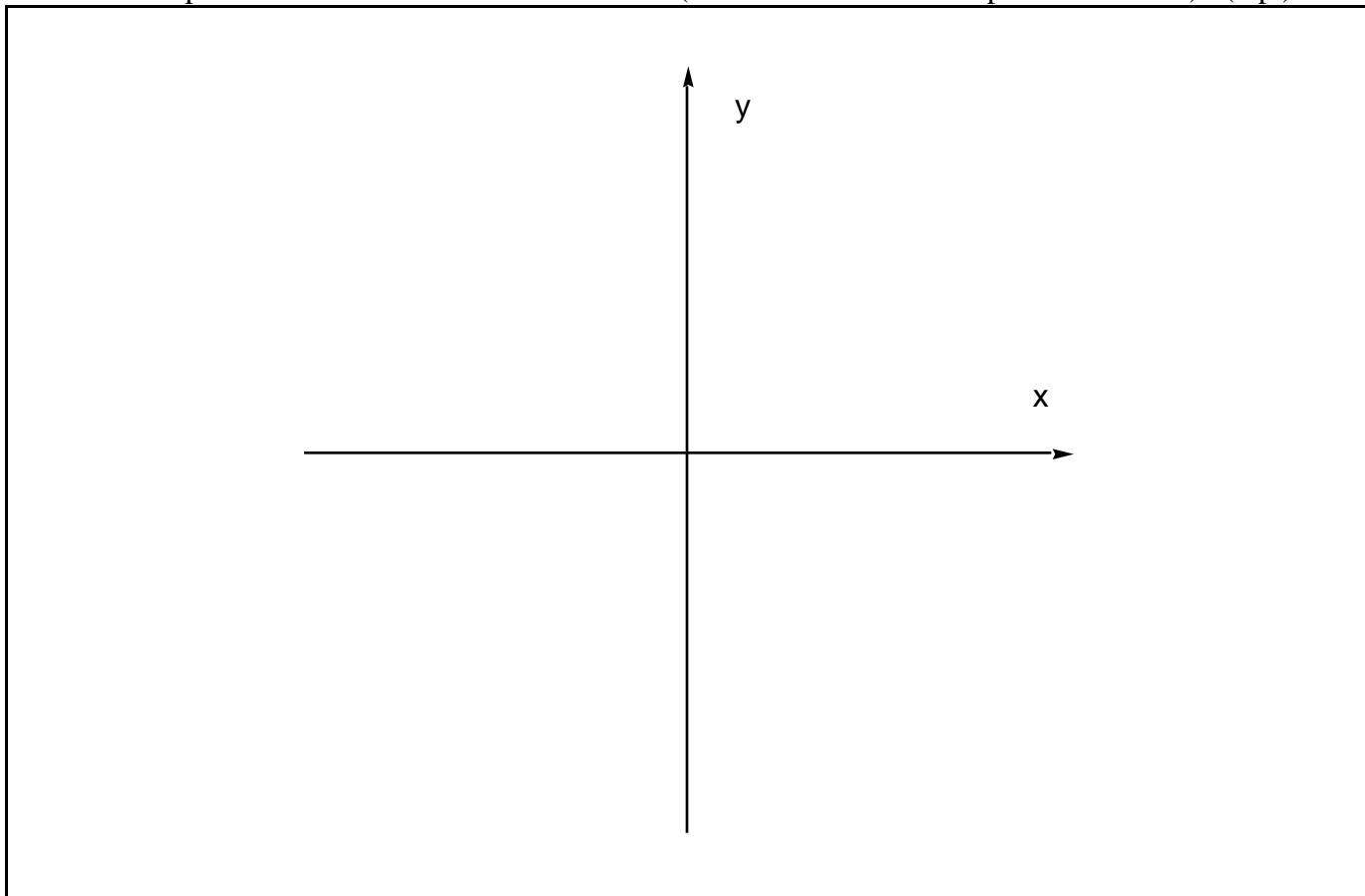
At what wave number would you expect the CO stretching band to occur in a primary amide? Does the computation over- or underestimate this vibrational frequency? Estimate the percentage of the error in this case. (5 p.)

(c) Bending Modes. (8 points)

Among the computed normal modes, identify the **in-plane bending mode** with the highest IR intensity. This mode is mode number _____ and it has wave number _____ 1/cm. Draw the displacement vector of this normal mode.

y

x
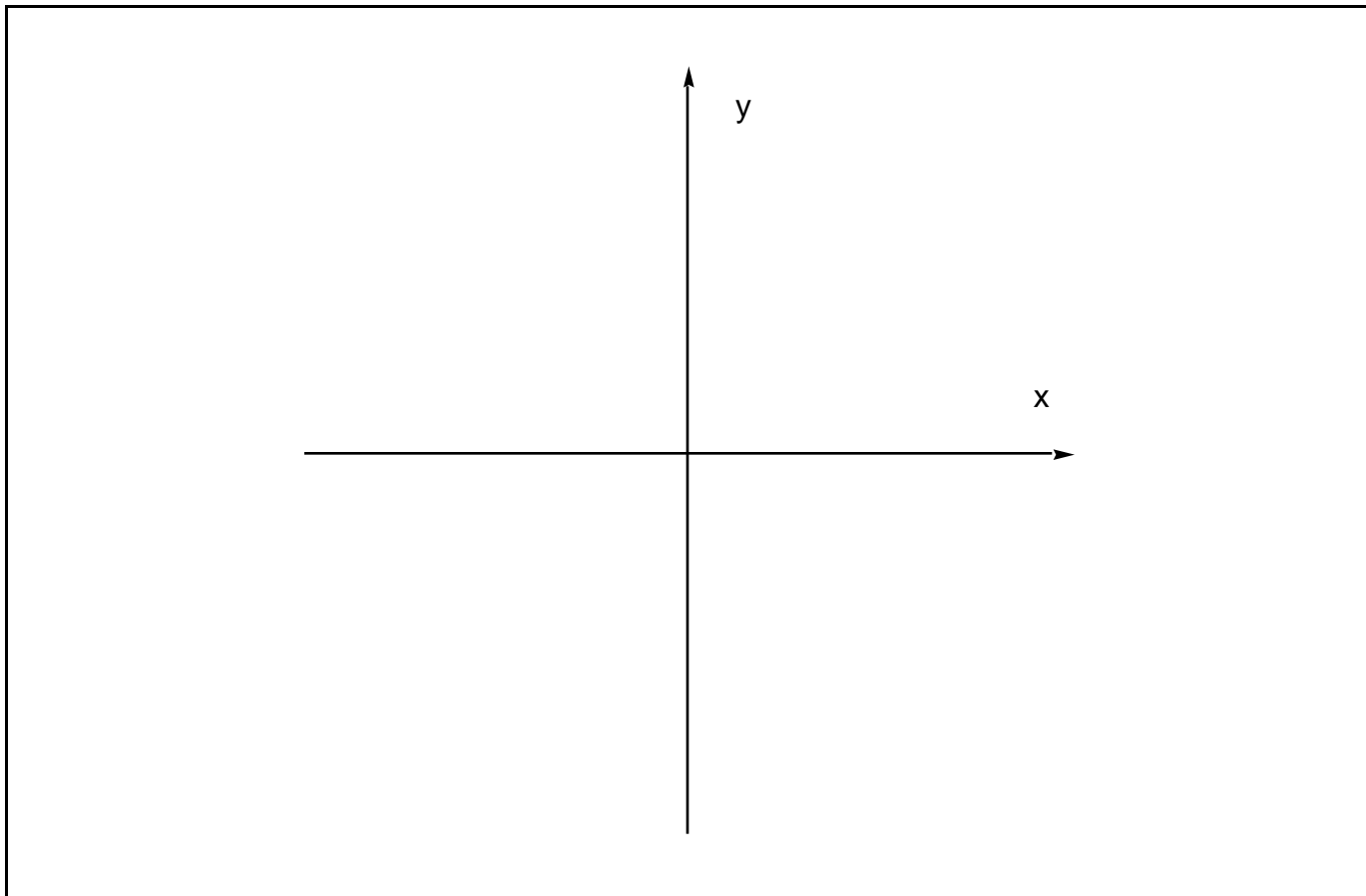
(d) The Stretching Modes Involving Hydrogen. (12 points)

Let's turn to the vibrations with the three highest frequencies. Inspect their computed normal modes and assign these bands. As appropriate, state whether the mode is "symmetric" or "antisymmetric".

3214 1/cm
3838 1/cm
3972 1/cm

The End of Another Superb Learning Experience!

```
   **************************************
   Gaussian 94:  SGI-G94RevC.3 26-Sep-1995
               23-Nov-1997
   **************************************
   ---------------------------------------------
   # RHF/6-31G* guess=read geom=checkpoint freq
   ---------------------------------------------
   ---------------------------------------------
   Formamide, RHF/6-31G*, planar, frequencies
   ---------------------------------------------
   Redundant internal coordinates taken from checkpointfile:
   /itchy-tmp/amide.chk
      Charge = 0 Multiplicity = 1
   C,0,0.,0.4154619163,0.
   O,0,1.1802424479,0.2425679724,0.
   H,0,-0.4438188256,1.4118387066,0.
   N,0,-0.9247582012,-0.5659197924,0.
   H,0,-0.6271149404,-1.5158980077,0.
   H,0,-1.8976984088,-0.3678174291,0.
```

   GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad
   GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

```
                    Input orientation:
   ---------------------------------------------------------------
   Center    Atomic            Coordinates (Angstroms)
   Number    Number        X          Y          Z
   ---------------------------------------------------------------
      1        6         0.000000   0.415462   0.000000
      2        8         1.180242   0.242568   0.000000
      3        1        -0.443819   1.411839   0.000000
      4        7        -0.924758  -0.565920   0.000000
      5        1        -0.627115  -1.515898   0.000000
      6        1        -1.897698  -0.367817   0.000000
   ---------------------------------------------------------------
                    Distance matrix (angstroms):
                  1          2          3          4          5
    1  C    0.000000
    2  O    1.192839   0.000000
    3  H    1.090753   2.001192   0.000000
    4  N    1.348439   2.254924   2.035395   0.000000
    5  H    2.030622   2.521655   2.933469   0.995515   0.000000
    6  H    2.052994   3.137880   2.298030   0.992903   1.712446
                  6
    6  H    0.000000
                    Interatomic angles:
       O2-C1-H3=122.3437      O2-C1-N4=124.9645      H3-C1-N4=112.6918
       O2-H3-N4= 67.9149      O2-C1-H5= 99.6547      H3-C1-H5=138.0016
       H3-O2-H5= 79.9671      C1-N4-H5=119.3049      O2-N4-H5= 93.6142
       H3-N4-H5=148.9358      O2-C1-H6=149.2375      H3-C1-H6= 88.4187
       O2-H3-H6= 93.4943      C1-N4-H6=121.7897      O2-N4-H6=147.4804
       H3-N4-H6= 92.1588      C1-H5-H6= 65.8882      O2-H5-H6= 93.685
       H3-H6-H5= 92.8536      H5-N4-H6=118.9054
   Stoichiometry     CH3NO
   Framework group   CS[SG(CH3NO)]
   Deg. of freedom    9
   Full point group                  CS        NOp    2
   Largest Abelian subgroup          CS        NOp    2
```

Largest concise Abelian subgroup C1   NOp   1
                    Standard orientation:

Center   Atomic   Coordinates (Angstroms)
Number   Number   X   Y   Z
----
   1   6   0.000000   0.415462   0.000000
   2   8   1.180242   0.242568   0.000000
   3   1   -0.443819   1.411839   0.000000
   4   7   -0.924758   -0.565920   0.000000
   5   1   -0.627115   -1.515898   0.000000
   6   1   -1.897698   -0.367817   0.000000

Rotational constants (GHZ):   75.6280039   11.6020648   10.0589283
Isotopes: C-12,O-16,H-1,N-14,H-1,H-1
Standard basis: 6-31G(d) (6D, 7F)
There are   39 symmetry adapted basis functions of A' symmetry.
There are   12 symmetry adapted basis functions of A" symmetry.
   51 basis functions   96 primitive gaussians
   12 alpha electrons   12 beta electrons
      nuclear repulsion energy   72.0740783340 Hartrees.
SCF Done: E(RHF) = -168.930702680   A.U. after   1 cycles
           Convg =   0.8342D-09   -V/T = 2.0020
           S**2   =   0.0000

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
                       A"   A'   A"
Frequencies --   110.5125   617.7250   673.4464
Red. masses --   1.2216   2.5012   1.1964
Frc consts --   0.0088   0.5623   0.3197
IR Inten   --   335.1842   17.2886   32.2897
Raman Activ --   0.8998   1.4156   0.2773
Depolar   --   0.7500   0.6410   0.7500
Atom AN   X   Y   Z   X   Y   Z   X   Y   Z
  1   6   0.00   0.00   0.01   0.07 -0.19   0.00   0.00   0.00 -0.10
  2   8   0.00   0.00   0.02   0.13   0.18   0.00   0.00   0.00   0.06
  3   1   0.00   0.00   0.00   -0.05 -0.24   0.00   0.00   0.00 -0.23
  4   7   0.00   0.00 -0.13   -0.15 -0.04   0.00   0.00   0.00   0.05
  5   1   0.00   0.00   0.53   -0.73 -0.22   0.00   0.00   0.00 -0.77
  6   1   0.00   0.00   0.84   -0.05   0.50   0.00   0.00   0.00   0.58
                        4   5   6
                       A'   A"   A'
Frequencies -- 1160.3308   1182.7659   1378.7805
Red. masses --   1.7818   1.5679   2.6744
Frc consts --   1.4134   1.2923   2.9955
IR Inten   --   8.3349   2.5120   154.9851
Raman Activ --   4.1302   6.1096   1.9304
Depolar   --   0.3732   0.7500   0.2005
Atom AN   X   Y   Z   X   Y   Z   X   Y   Z
  1   6   0.05   0.04   0.00   0.00   0.00   0.21   0.07   0.30   0.00
  2   8   0.12   0.03   0.00   0.00   0.00 -0.06   0.00 -0.04   0.00
  3   1   0.31   0.14   0.00   0.00   0.00 -0.96   0.21   0.37   0.00
  4   7   -0.20 -0.03   0.00   0.00   0.00 -0.04   -0.03 -0.21   0.00
  5   1   0.40   0.14   0.00   0.00   0.00 -0.14   -0.69 -0.43   0.00
  6   1   -0.35 -0.73   0.00   0.00   0.00 -0.01   0.03   0.12   0.00

```
                          7                           8                           9
                          A'                          A'                          A'
Frequencies --    1563.5119                   1789.2391                   1998.9666
Red. masses --       1.2230                      1.2200                      7.2925
Frc consts  --       1.7615                      2.3012                     17.1687
IR Inten    --      10.3329                     84.1360                    514.9811
Raman Activ --       6.3519                      4.3854                      8.9590
Depolar     --       0.4381                      0.6567                      0.3716
Atom AN      X       Y       Z        X       Y       Z        X       Y       Z
  1   6   -0.01   -0.08    0.00     0.02   -0.04    0.00     0.61   -0.02    0.00
  2   8   -0.08    0.05    0.00    -0.04    0.01    0.00    -0.37    0.05    0.00
  3   1    0.93    0.31    0.00     0.07   -0.03    0.00    -0.34   -0.44    0.00
  4   7    0.02   -0.02    0.00     0.07    0.09    0.00    -0.10   -0.02    0.00
  5   1    0.06    0.00    0.00    -0.65   -0.13    0.00     0.38    0.12    0.00
  6   1    0.06    0.15    0.00    -0.09   -0.73    0.00    -0.10    0.00    0.00
                         10                          11                          12
                          A'                          A'                          A'
Frequencies --    3214.1861                   3838.0702                   3972.6012
Red. masses --       1.0894                      1.0471                      1.1061
Frc consts  --       6.6313                      9.0879                     10.2845
IR Inten    --     103.8155                     57.9515                     63.4500
Raman Activ --      95.3043                     79.6140                     43.6507
Depolar     --       0.2930                      0.1360                      0.7245
Atom AN      X       Y       Z        X       Y       Z        X       Y       Z
  1   6    0.03   -0.08    0.00     0.00    0.00    0.00     0.00    0.00    0.00
  2   8    0.00    0.00    0.00     0.00    0.00    0.00     0.00    0.00    0.00
  3   1   -0.39    0.92    0.00     0.00    0.00    0.00     0.00    0.01    0.00
  4   7    0.00    0.00    0.00     0.03    0.05    0.00     0.07   -0.05    0.00
  5   1    0.00   -0.01    0.00     0.23   -0.74    0.00    -0.18    0.59    0.00
  6   1    0.01   -0.02    0.00    -0.61    0.13    0.00    -0.76    0.16    0.00


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- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Atom  1 has atomic number  6 and mass  12.00000
Atom  2 has atomic number  8 and mass  15.99491
Atom  3 has atomic number  1 and mass   1.00783
Atom  4 has atomic number  7 and mass  14.00307
Atom  5 has atomic number  1 and mass   1.00783
Atom  6 has atomic number  1 and mass   1.00783
Molecular mass:    45.02146 amu.
Principle axes and moments of inertia in atomic units:
                          1         2         3
    EIGENVALUES --    23.86340 155.55345 179.41684
          X            0.92578  -0.37807   0.00000
          Y            0.37807   0.92578   0.00000
          Z            0.00000   0.00000   1.00000
THIS MOLECULE IS AN ASYMMETRIC TOP.
ROTATIONAL SYMMETRY NUMBER  1.
ROTATIONAL TEMPERATURES (KELVIN)      3.62955    0.55681    0.48275
ROTATIONAL CONSTANTS (GHZ)           75.62800   11.60206   10.05893
Zero-point vibrational energy     128599.4 (Joules/Mol)
                                   30.73599 (Kcal/Mol)
WARNING-- EXPLICIT CONSIDERATION OF   2 DEGREES OF FREEDOM AS
         VIBRATIONS MAY CAUSE SIGNIFICANT ERROR
VIBRATIONAL TEMPERATURES:     159.00    888.76    968.93   1669.45   1701.73
       (KELVIN)              1983.75   2249.53   2574.30   2876.05   4624.47
```

```
Zero-point correction=                           0.048981 (Hartree/Particle)
Thermal correction to Energy=                    0.052854
Thermal correction to Enthalpy=                  0.053798
Thermal correction to Gibbs Free Energy=         0.024049
Sum of electronic and zero-point Energies=        -168.881722
Sum of electronic and thermal Energies=           -168.877849
Sum of electronic and thermal Enthalpies=         -168.876905
Sum of electronic and thermal Free Energies=      -168.906653
```

	E	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	33.166	10.438	62.612
ELECTRONIC	0.000	0.000	0.000
TRANSLATIONAL	0.889	2.981	37.339
ROTATIONAL	0.889	2.981	21.126
VIBRATIONAL	31.389	4.477	4.146
VIBRATION 1	0.606	1.941	3.260
VIBRATION 2	0.977	0.994	0.420

	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.867196D-11	-11.061883	-26.455159
TOTAL V=0	0.293510D+12	11.467624	25.420947
VIB (BOT)	0.790570D-22	-22.102060	-50.891873
VIB (BOT) 1	0.185310D+01	0.267898	0.616858
VIB (BOT) 2	0.237311D+00	-0.624683	-1.438385
VIB (V=0)	0.267576D+01	0.427447	0.984233
VIB (V=0) 1	0.241937D+01	0.383702	0.883506
VIB (V=0) 2	0.105346D+01	0.022617	0.052079
ELECTRONIC	0.100000D+01	0.000000	0.000000
TRANSLATIONAL	0.118738D+08	7.074590	16.289845
ROTATIONAL	0.923819D+04	3.965587	9.131101

```
Item              Value     Threshold  Converged?
Maximum Force     0.000067   0.000450     YES
RMS     Force     0.000030   0.000300     YES
Maximum Displacement  0.000712  0.001800  YES
RMS     Displacement  0.000374  0.001200  YES
Predicted change in Energy=-4.635637D-08
Optimization completed.
   -- Stationary point found.
```

THERE'S SMALL CHOICE IN A BOWL OF ROTTEN APPLES.
                    SHAKESPEARE
```
Job cpu time:  0 days  0 hours  1 minutes 17.2 seconds.
Normal termination of Gaussian 94
```