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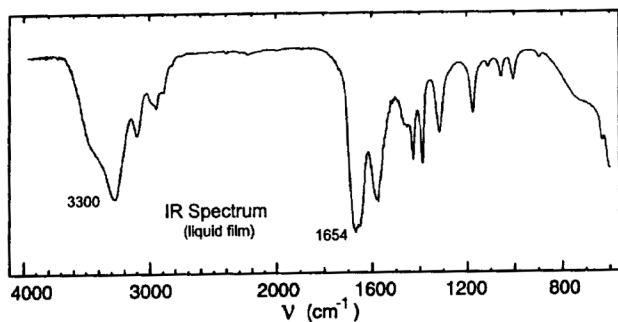
Third 1-Hour Examination
"Vibrational Spectroscopy"

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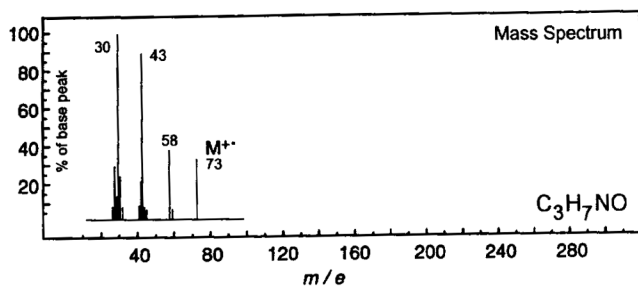
Name:

    Answer Key

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

% of base peak

C_3H_7NO

No significant UV
absorption above 220 nm

^{13}C NMR Spectrum
(50.0 MHz, CDCl$_3$ solution)

DEPT   CH$_2$↓ CH$_3$↑ CH↑

solvent

proton decoupled

^1H NMR Spectrum
(200 MHz, CDCl$_3$ solution)

expansion
with irradiation (decoupling)
at δ 7.4 ppm

expansion

exchanges
with D$_2$O on warming

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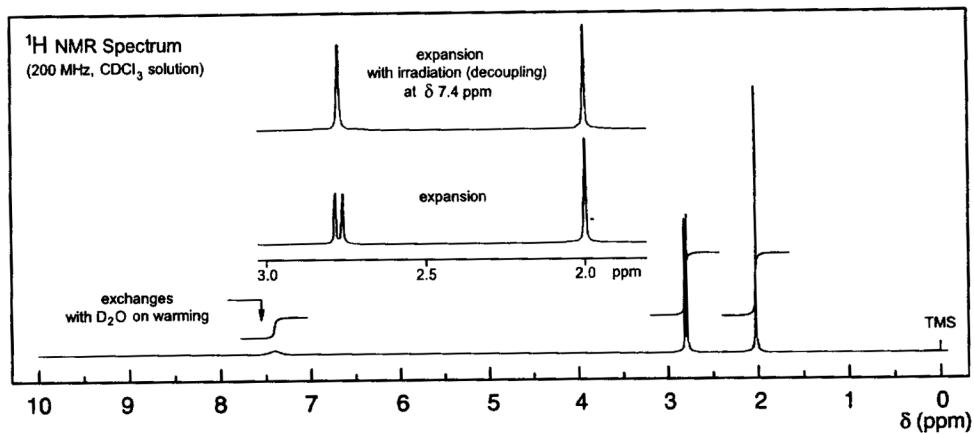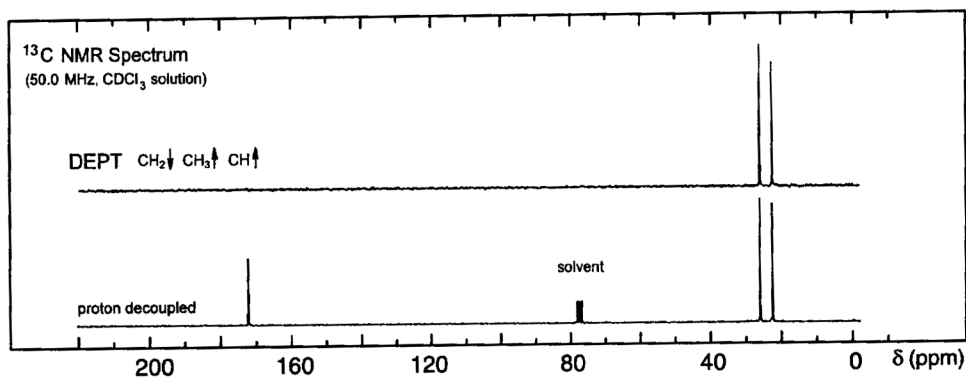
(a) Draw the **structure** and give the correct **name** of the unknown. (9 points)

Me-NH-CO-Me   *N*-methyl-acetamide

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

sym. and asym. methyl-CH stretches from the *N*-methyl

sym. and asym. methyl-CH stretches from the *C*-methyl (lower freq. compared to *N*-methyl).

the N-H stretch (highest freq.)

(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)

Amide I (mostly the CO stretch) 1640 -1670

Amide II (CO stretch and some NH stretch) 1620 - 1650   (amide needs at least one H)

Amide from ammonia or primary amine.

(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)

The NH would be sharp as it is no longer engaged in H-bonding.

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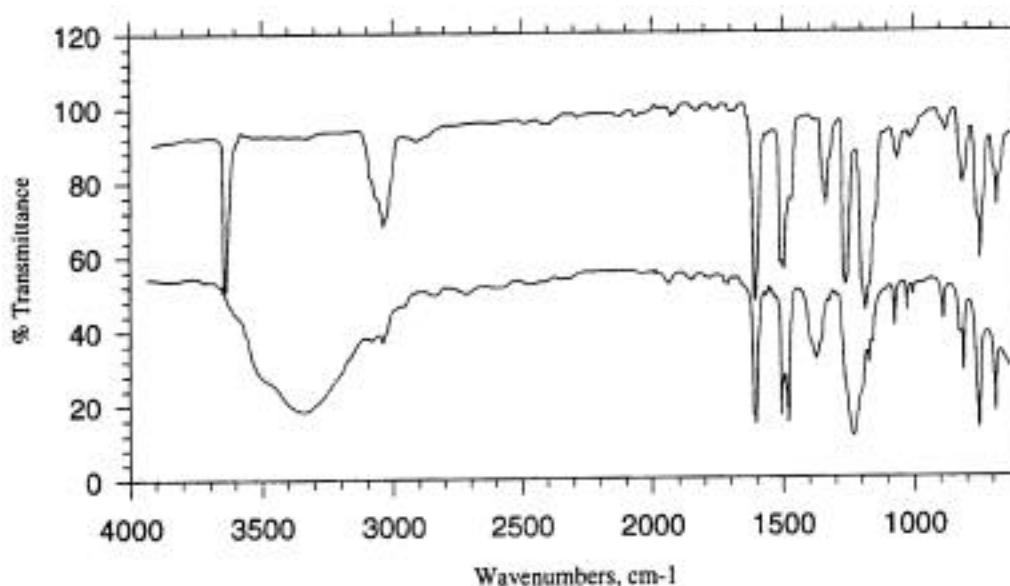
The IR spectra are shown of **phenol**. One of the spectra was recorded fort a **liquid film** of phenol and the other spectrum is the **vapour phase** spectrum.

(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)

In condensed phase, the OH stretch is shifted bathochromically and broadens.
H-bonding weakens the H-O bond.
Drawing should show intermolecular H-bonding. (Dimers are NOT likely.)

Question 3. Hydrocarbon Spectrum. (11 points)
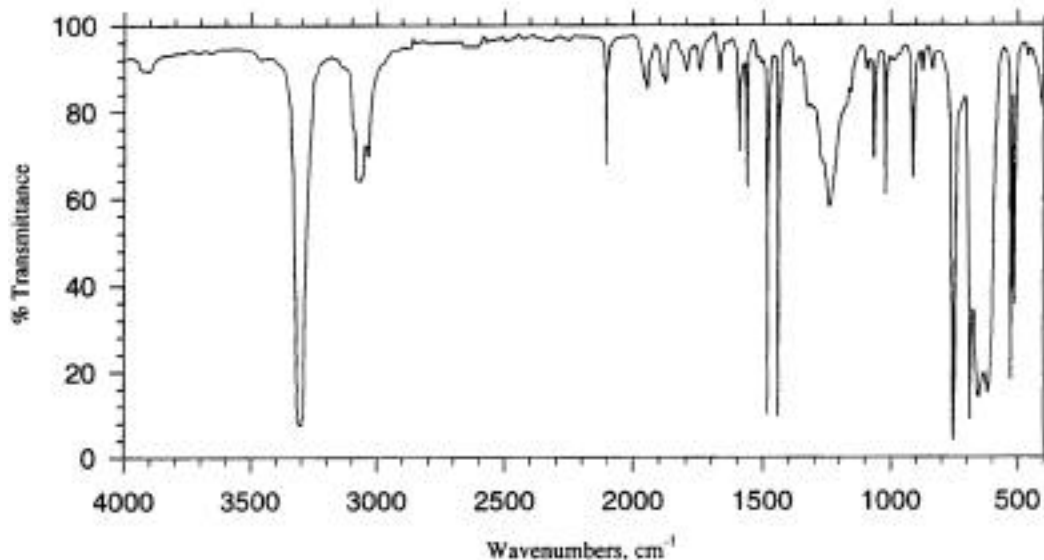
(a) The IR spectrum is shown of **phenylacetylene**. Draw the structure of this compound. (2 points)

Well, ...

(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)

There are the sym. and the asym. stretches or aromatic C-H. One stretch for acetylene C-H.
associated with the acetylene C-H (stonger) and the benzene C-H (waeker).
Argue about the hybridization.

(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)
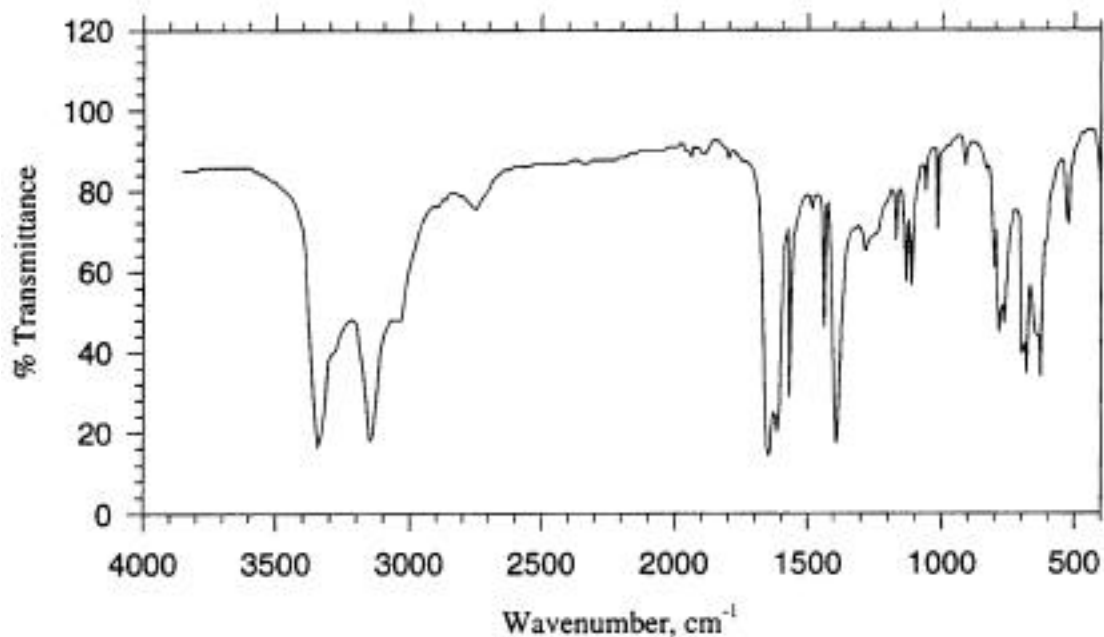
(a) Analyze the IR spectrum shown and determine what type of compound is consistent with this spectrum. You do not need to provide the structure of the actual compound for which this spectrum was recorded. Rather, it is the goal to recognize the functional group. You do need to argue which bands are characteristic for that functional group.

-CO-NH2

The two sharp peaks above 3100 are sym. and asym. NH stretches
The peaks around 1600 are amine I and amide II

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).
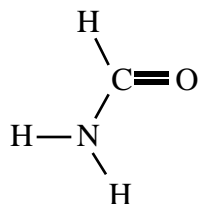
(a) The Amino Inversion.

Draw the displacement vector of the normal mode with the lowest vibrational frequency in the space below. (5 points)
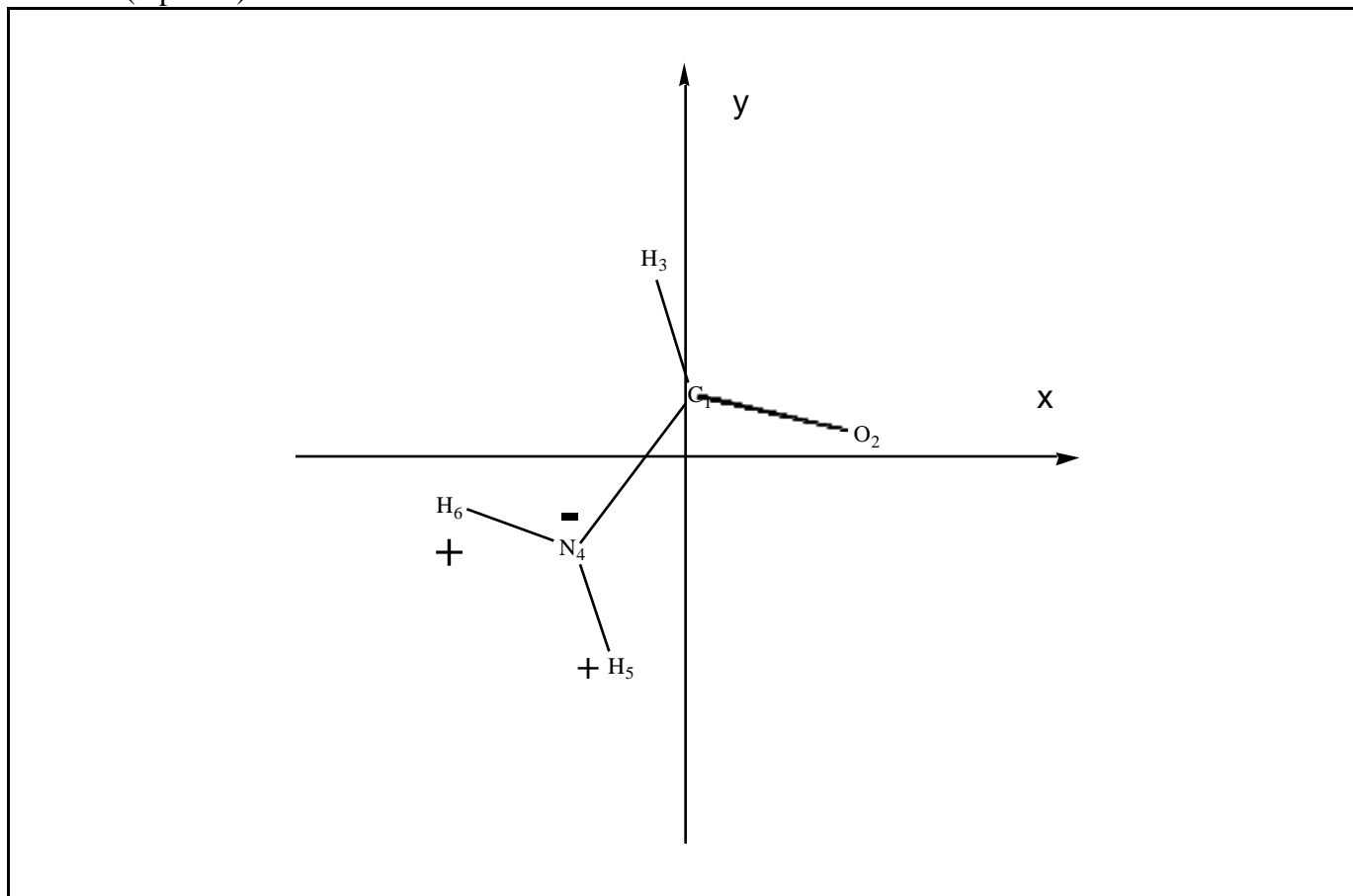
(b) The "CO Stretch". (15 points)

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 __**1999**___ 1/cm. (5 points)

Draw the displacement vector of this normal mode (and note that it is not a pure CO stretch). (5 p.)
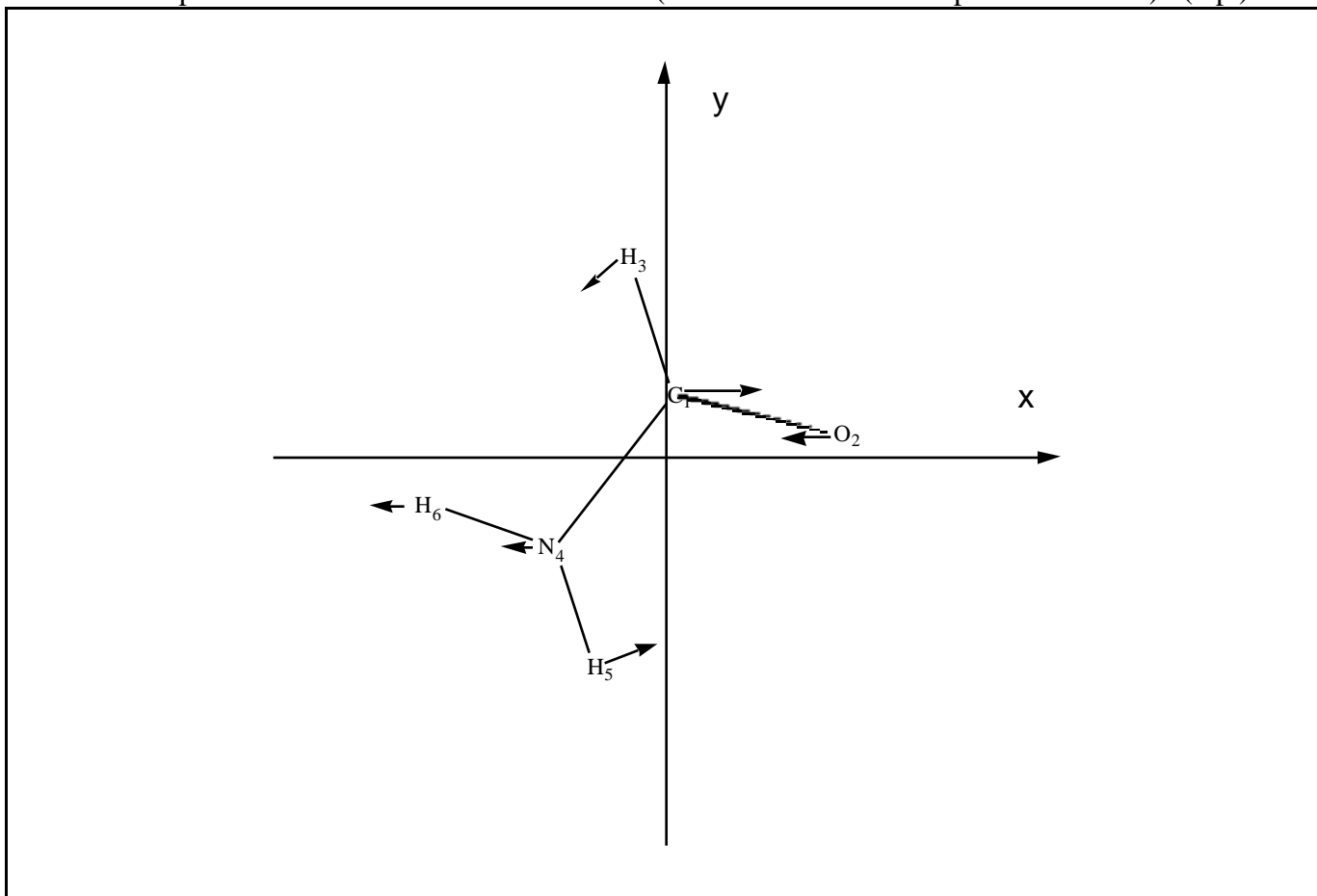
At what wave number would you expect the CO stretching band to occur in a primary amide? Does the computation over- or underestimate this vibrational frequency? Estimate the percentage of the error in this case. (5 p.)

1640 - 1670 1/cm for the "amide I"
based on the average value of 1655 1/cm,
the computation is 345 1/cm or 21% too high!!

(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 __**6**__ and it has wave number __**1379**__ 1/cm. Draw the displacement vector of this normal mode.
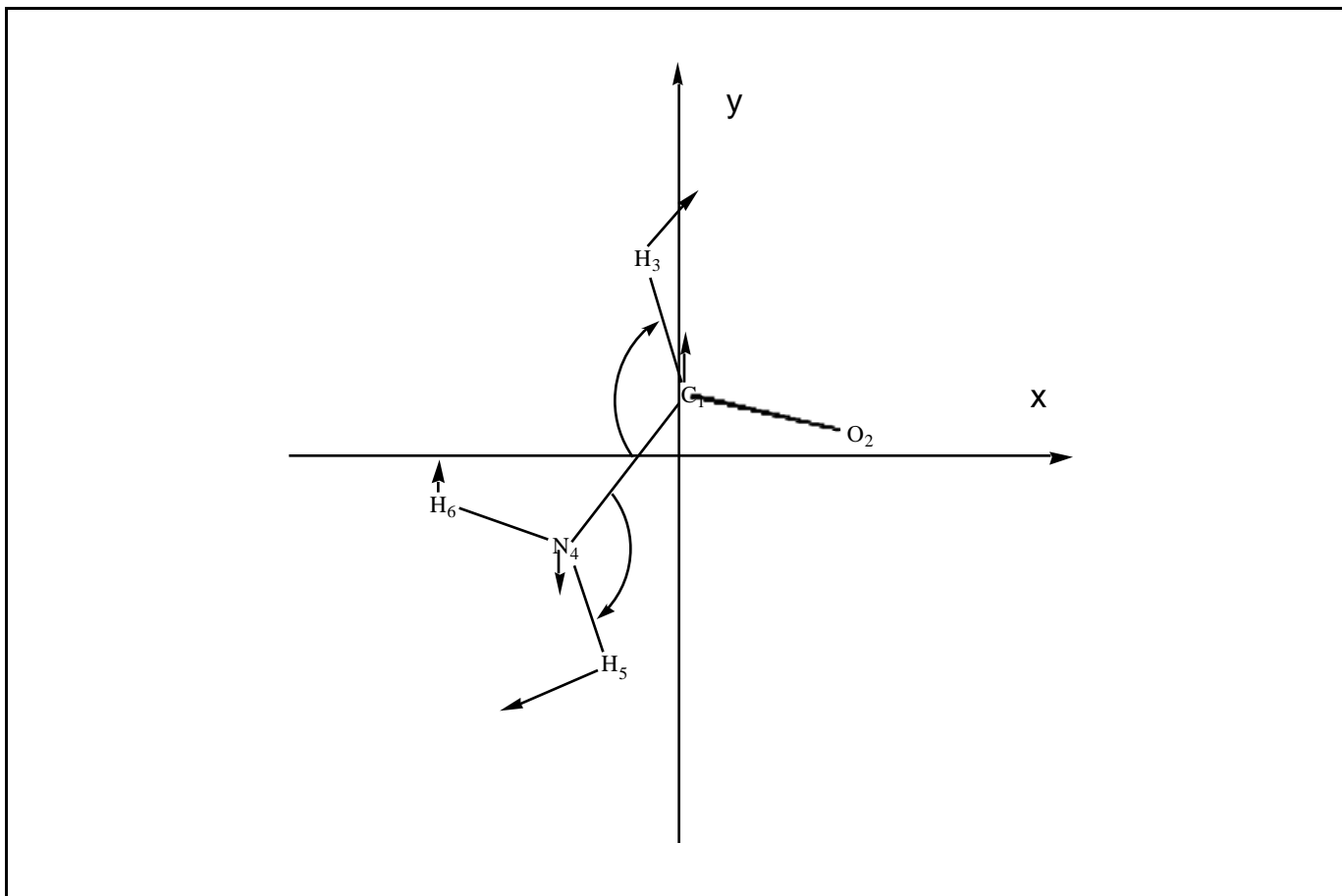
(d) The Stretching Modes Involving Hydrogen. (12 points)

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	
	The CH stretch
3838 1/cm	
	The amino groups **symmetric** stretching mode
3972 1/cm	
	The amino groups **asymmetric** stretching mode

The End of Another Superb Learning Experience!

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*************************************
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
```