Name:

Answer Key

<table>
<thead>
<tr>
<th>Question 1 (Combination)</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Question 2 (Environment)</td>
<td>14</td>
</tr>
<tr>
<td>Question 3 (Hydrocarbons)</td>
<td>11</td>
</tr>
<tr>
<td>Question 4 (Functionality)</td>
<td>10</td>
</tr>
<tr>
<td>Question 5 (Normal Modes)</td>
<td>40</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
Question 1. Combination Problem. (25 points)
(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 for 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.)
(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 \( \text{cm}^{-1} \). 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 (stronger) and the benzene C-H (weaker).

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).

![Formamide structure](image)

(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 \( 1999 \) \text{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 \text{1/cm} for the “amide I”

based on the average value of 1655 \text{1/cm},
the computation is 345 \text{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”.

<table>
<thead>
<tr>
<th>Frequency (1/cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3214</td>
<td>The CH stretch</td>
</tr>
<tr>
<td>3838</td>
<td>The amino groups <strong>symmetric</strong> stretching mode</td>
</tr>
<tr>
<td>3972</td>
<td>The amino groups <strong>asymmetric</strong> stretching mode</td>
</tr>
</tbody>
</table>

The End of Another Superb Learning Experience!
# 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:

<table>
<thead>
<tr>
<th>Center</th>
<th>Atomic Number</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number</td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0.000000</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>1.180242</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-0.443819</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>-0.924758</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-0.627115</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1.897698</td>
</tr>
</tbody>
</table>

Distance matrix (angstroms):

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.192839</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.090753</td>
<td>2.001192</td>
<td>0.000000</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.348439</td>
<td>2.254924</td>
<td>2.035395</td>
<td>0.000000</td>
</tr>
<tr>
<td>5</td>
<td>2.030622</td>
<td>2.521655</td>
<td>2.933469</td>
<td>0.995515</td>
</tr>
<tr>
<td>6</td>
<td>2.052994</td>
<td>3.137880</td>
<td>2.298030</td>
<td>0.992903</td>
</tr>
</tbody>
</table>

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  C1-N4-H6=121.7897  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= 92.9536  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

Standard orientation:

Center | Atomic Number | Number | Coordinates (Angstroms) | X     | Y     | Z     |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0.000000</td>
<td>0.415462</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>1.180242</td>
<td>0.242568</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-0.443819</td>
<td>1.411839</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>-0.924758</td>
<td>-0.565920</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-0.627115</td>
<td>-1.515898</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1.897698</td>
<td>-0.367817</td>
<td>0.000000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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:

<table>
<thead>
<tr>
<th>Atom AN</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0.05</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.21</td>
<td>0.07</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.12</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.06</td>
<td>0.00</td>
<td>-0.04</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.31</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.96</td>
<td>0.21</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>-0.20</td>
<td>-0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.04</td>
<td>-0.03</td>
<td>-0.21</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.40</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.14</td>
<td>-0.69</td>
<td>-0.43</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-0.35</td>
<td>-0.73</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.01</td>
<td>0.03</td>
<td>0.12</td>
</tr>
</tbody>
</table>
--- 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:

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>0.92578</td>
<td>-0.37807</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.37807</td>
<td>0.92578</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
<td>1.00000</td>
</tr>
</tbody>
</table>

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