Q1.

(Z-MATRIX STRUCTURE A)
$BASIS GBASIS=N31 NGAUSS=6 POLAR=POPN31 NDFUNC=1 $END
$DATA
OPTIMIZATION Z-MATRIX COORDINATES OF (A)
C1 1
H1
C1 1 rCH
O1 2 rCO2 1 -aHCO
H2 3 rOH 2 aHCO 1 dXOCO1
O2 2 rCO1 3 aHCO 4 dXOCO2

dXOCO1= 180
dXOCO2= 0
aHCO= 120
rCO1= 1.2
rCO2= 1.1
rCH= 1
rOH= 1

$END
(Z-MATRIX STRUCTURE B)
$BASIS GBASIS=N31 NGAUSS=6 POLAR=POPN31 NDFUNC=1 $END
$DATA
OPTIMIZATION Z-MATRIX COORDINATES OF (B)
C1 1
O2
C1 1 rCH
O1 2 rCO2 1 -aHCO
H2 3 rOH 2 aHCO 1 dXOCO1
H1 2 rCO1 3 aHCO 4 dXOCO2

dXOCO1= 180
dXOCO2= 0
aHCO= 120
rCO1= 1.2
rCO2= 1.1
rCH= 1
rOH= 1

$END
These z-matrices were optimized by RUNTYP=OPTIMIZE.
(OPTIMIZED Z-MATRIX STRUCTURE A)

H1
C1 1 1.0834095
O1 2 1.3227180 1 110.4006671
H2 3 0.9533284 2 108.7104614 1 180.0000000 0
O2 2 1.1818802 3 124.8699536 4 0.0000000 0

(OPTIMIZED Z-MATRIX STRUCTURE B)
O2
C1 1 1.1756684
O1 2 1.3282834 1 122.9865612
H2 3 0.9481608 2 111.5390045 1 180.0000000 0
H1 2 1.0899920 3 113.8685930 4 0.0000000 0

Frequency calculations were done by RUNTYP=HESSIAN. Under the heading normal mode calculation, we can see that the frequencies are calculated. Because these points form a minima, the frequencies all are real and not imaginary.

Q2.

From above calculations, Hartree Fock energy for

STRUCTURE A= -188.762309 Hartree= -118446.914 kcal/mol (more stable)
STRUCTURE B= -188.752546 Hartree= -118440.788 kcal/mol (less stable)
Energy difference (B-A) = 6.126 kcal/mol

(For each frequency, energy associated = $0.00024*0.5*6.022*10^{-23}*6.62*10^{-34}*3*10^{8}*$ Freq.(cm^{-1}) kcal/mol)

Frequencies for structure A (cm^{-1}) = 3.631, 0.946, 0.362, 0.021, 0.718, 1.084, 691.842, 715.409, 1192.250, 1274.533, 1440.064, 1552.388, 2035.080, 3320.491, 4041.382

ZPE for A= 0.2339 kcal/mol

Frequencies for structure B (cm^{-1}) = 3.725, 0.146, 0.099, 0.016, 2.840, 9.579, 517.809, 724.335, 1179.114, 1237.221, 1425.708, 1583.007, 2080.085, 3228.363, 4106.772

ZPE for B= 0.2310 kcal/mol

ZPE difference (B-A)= -0.0029 kcal/mol

Thus, ZPE corrected Energy difference= 6.1231 kcal/mol

Q3.

Initial guess for transition state.

H1
C1 1 1.0712538
O1 2 1.3473865 1 110.4549223

H2 3 0.9473238 2 113.7428070 1 90.0000000 0
O2 2 1.2038858 3 124.5247985 4 -90.0000000 0

Hessian and gradient were calculated at this point by RUNTYP=HESSIAN and RUNTYP=GRADIENT. The gradient calculated was greater than 0.0001 and the force constant matrix had negative eigen vectors which shows that it has correct structure for transition state optimization.

Q4.

The guessed ZMT for T.S was used to find the saddle point and was later optimized using Newton-Raphson method with hessian calculated at this geometry with HESS=CALC. Same final state is observed in cartesian coordinates.

OPTIMIZED T.S ZMT
H1
C1 1 1.0872320
O1 2 1.3508087 1 113.0253154
H2 3 0.9503670 2 111.9969161 1 86.4676134 0
O2 2 1.1743913 3 123.9491716 4 -95.9996544 0

Here, I observe that the initial dihedral angles I guessed for H2 and O2 are different. They differ by about 5 degrees.

Q.5

On frequency calculation at the optimized point, we find one imaginary frequency indicating that it is a transition state.
Hartree Fock energy for T.S= -188.740755 Hartree= -118433.389 kcal/mol
ZPE of T.S= 0.2197 kcal/mol

Energy barrier for A (TS-A)= 13.525 kcal/mol
ZPE corrected Energy difference= 13.5108 kcal/mol
Energy barrier for B (TS-B)= 7.399 kcal/mol
ZPE corrected Energy difference= 7.3877 kcal/mol

Q.6

A lot effort were put to figure out how to carry-out the IRC calculation. Unfortunately, although I could make the input file execute some IRC calculation, I was not able to extract any meaningful information from its log file.

! A2. Q6. T.S STRUCTURE IN 6-31G* BY HF
$CONTRL SCFTYP=RHF RUNTYP=IRC COORD=ZMT MULT=1 ICHARG=0 NZVAR=9 $END
$BASIS GBASIS=N31 NGAUSS=6 POLAR=POPN31 NDFUNC=1 $END
$STATPT HESS=CALC METHOD=NR $END
$DATA
Z-MATRIX COORDINATES OF (T.S) (AFTER SADPOINT CAL)

```
C1 1
 H1
 C1    1   1.0872320
 O1    2   1.3508087  1   113.0253154
 H2    3   0.9503670  2   111.9969161  1    86.4676134  0
 O2    2   1.1743913  3   123.9491716  4   -95.9996544  0

 $END
 $IRC PACE=LINEAR STRIDE=0.0001 NPOINT=75 IFREEZ(1)=1,2,3 IFREEZ(2)=1,2,3,4,5,6
IFREEZ(5)=1,2,3 SADDLE=TRUE FORWARD=TRUE $END
```