CHEM442-001/002 Name ________________________________
College of Charleston
Spring 2001
Exam V Score ___________ /100

1(50). The rotational and rotational-vibrational spectra for carbon monoxide ($^{12}C^{16}O$), where $M/(g\ mol^{-1})$ = 12.00000 and 15.99491, were analyzed.
If the rotational spectroscopic constant for CO is $B_e = 1.9302\ cm^{-1}$, calculate the C≡O bond length.

Predict the location (wave numbers) of the first four lines of the pure rotational spectrum.

Calculate B^* and determine the intensity ratio of $I(J{=}2)/I(J{=}1)$ at 25 °C.

For the vibrational transition $v = 0 \leftrightarrow 1$, the values of the wave numbers of the P and R branches can be fit to the equation

$$\tilde{\nu}/(\mathrm{cm^{-1}}) = \tilde{\nu}_o + (2B_e - 2\alpha_e)m - \alpha_e m^2$$
$$= (2143.273) + (3.8264)m - (0.01754)m^2$$

using a nonlinear multiple least squares regression technique. Determine B_e and α_e from these results.

Using the empirical equation given above, derive an equation expressing $\Delta\tilde{\nu}$ for m changing from m to m+1.

Calculate the separation of lines in the P branch for J=10 (m=-10) and in the R branch for J=10 (m=11).

2(20). The rotational-vibrational spectrum of carbon dioxide ($^{16}O{=}^{12}C{=}^{16}O$) was analyzed.
The symmetry of the vibrational modes can be determined to be E_{1u}, A_{2u}, and A_{1g}. Using the character table for the $\mathbf{D}_{\infty h}$ point group, determine which transition(s) is/are infrared active _______________ and Raman active ______________ .

$\mathbf{D}_{\infty h}$ representation	$\hat{E}$	$2\hat{C}_\infty^\phi$	$\infty\hat{\sigma}_v$	$\hat{i}$	$\hat{\sigma}_h$	$2\hat{S}_\infty^\phi$	$\infty\hat{C}_2$	
A_{1g}	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{1u}	1	1	1	-1	-1	-1	-1	
A_{2g}	1	1	-1	1	1	1	-1	R_z
A_{2u}	1	1	-1	-1	-1	-1	1	z

E_{1g}	2	2 cos ϕ	0	2	-2	2 cos ϕ	0	(R_x,R_y), (xz,yz)
E_{1u}	2	2 cos ϕ	0	-2	2	2 cos ϕ	0	(x,y)
E_{2g}	2	2 cos 2ϕ	0	2	2	2 cos 2ϕ	0	(x^2-y^2,xy)
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	

To change the symmetry of the CO_2 molecule, a student proposed substituting ^{18}O for one of the O atoms to study the spectrum of $^{18}O{=}^{12}C{=}^{16}O$. Circle the correct response to each change in property of the new molecule compared to the original $^{16}O{=}^{12}C{=}^{16}O$:

$^{18}O{=}^{12}C$ bond length: increased identical decreased

$^{18}O{=}^{12}C$ bond strength: increased identical decreased

moment of inertia increased identical decreased

$\Delta\tilde{\nu}$ in the Raman S branch: increased identical decreased

3(30). For the reaction

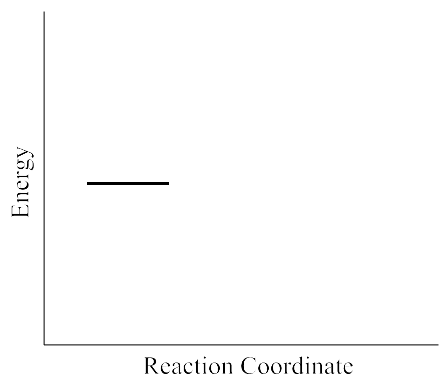
$$A \rightarrow B \quad \Delta_r E = -100 \text{ kJ}$$

there are two different proposed mechanisms

mechanism 1 with rate constant k_1 $A \rightarrow B$ $E_{a,1} = 50$ kJ mol^{-1}

mechanism 2 with rate constant k_2 $A \rightarrow B$ $E_{a,2} = 300$ kJ mol^{-1}

Draw the complete reaction coordinate diagram (to scale) showing both mechanisms. Clearly label the reactant, product, $\Delta_r E$, and activation energies.



Based on activation energies, which mechanism is preferred? _____

If the temperature is decreased from 25 °C to 0 °C, calculate the respective ratios of the rate constants $k_1(0\ °C)/k_1(25\ °C)$ and $k_2(0\ °C)/k_2(25\ °C)$.

For which mechanism is the greater temperature effect? _____

A plot of $1/C_B$ against t is linear during the early stages of the reaction and becomes nonlinear during and after the intermediate stages of the reaction and a plot of ln C_B against t is nonlinear during and before the intermediate stages of the reaction and becomes linear during the final stages of the reaction. On the other side of this sheet, write a brief interpretation of these observations.