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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

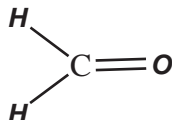
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1976

Final Examination
due May 14, 1976
(Late papers will not be accepted)

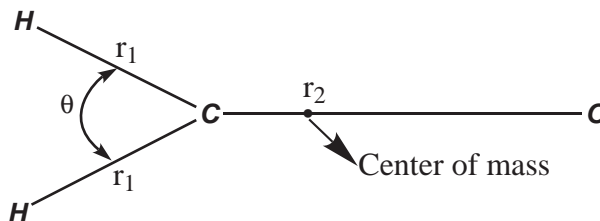
Answer all questions. Each part is worth 10 points, 120 points total.
Open book, open notes, no time limit, no collaboration, pocket calculators strongly recommended.
Good luck!
I never did like the smell of formaldehyde.

The formaldehyde molecule is planar and has two equal C–H bond lengths.



- A. Determine the point group for H_2CO and generate the character of the 12 dimensional reducible Cartesian representation. Reduce this representation and list the irreducible representation labels of the $3N-6$ vibrational degrees of freedom of H_2CO .
- B. Construct reducible representations using various internal coordinate basis functions. Which normal modes are *pure* stretching, in-plane bending, out-of-plane bending? Do not list modes that involve combinations of bending and stretching motions.
- C. Suppose we did not know that H_2CO was planar, but we were certain that the two CH bonds had equal lengths. Describe how you might use a comparison of the Infrared and Raman Vibrational Spectra to distinguish between the planar and nonplanar possibilities.
- D. The geometric structure of planar H_2CO is completely determined by three parameters:

$$r_1 = r_{\text{HC}}, r_2 = r_{\text{CO}}, \theta = \theta_{\text{HCH}}$$



The center of mass is on the C–O bond axis somewhere between the C and O atoms.

Define a coordinate system in which the origin is at the center of mass, the z -axis is along C–O, and the xz plane is the plane of the molecule. Express the coordinates of each atom in this system in terms of r_1 , r_2 , and θ .

- E.** Express the principal moments of inertia in terms of r_1 , r_2 , and θ . The principal axes (located by symmetry, labeled according to $I_a \leq I_b \leq I_c$) are:

$$\begin{aligned} I_a & \text{ (CO axis)} \\ I_b & \text{ (axis in molecular plane perpendicular to CO axis)} \\ I_c & \text{ (axis perpendicular to molecular plane).} \end{aligned}$$

- F.** Calculate I_a , I_b , and I_c for $\text{H}_2^{12}\text{C}^{16}\text{O}$, $\text{D}_2^{12}\text{C}^{16}\text{O}$, $\text{H}_2^{13}\text{C}^{16}\text{O}$, and $\text{H}_2^{12}\text{C}^{18}\text{O}$ using the following atomic masses.

H	1.008142 amu
D	2.014735
^{12}C	12.003804
^{13}C	13.007473
^{16}O	16.000000
^{18}O	18.004874

and estimated values for r_1 , r_2 , and θ :

$$\begin{aligned} \theta_{\text{HCH}} &= 117.6^\circ && \text{(from H}_2\text{C} = \text{CH}_2) \\ r_{\text{CH}} &= 1.086\text{\AA} && \text{(from H}_2\text{C} = \text{CH}_2) \\ r_{\text{CO}} &= 1.216\text{\AA} && \text{(from CH}_3\text{CHO).} \end{aligned}$$

You are free to make your own estimates, but please do not look up the actual structure of H_2CO and use “exact” values. You are going to use these calculations to assign the H_2CO microwave spectrum, therefore reasonably accurate structural estimates will be to your advantage.

Calculate

$$\Delta = I_c - I_a - I_b$$

for all four isotopes. This quantity is called the *inertial defect*. It is zero for planar molecules. Δ is the best test for planarity, especially when the state in question is electronically excited and a comparison of infrared and Raman Spectra is not possible.

- G.** For all four isotopic variations of part **F**, convert I_a , I_b , and I_c to the rotational constants A , B , C in units of $\text{MHz}(10^6\text{Hz})$.

$$A, B, C(\text{MHz}) = \frac{5.05376 \times 10^5}{I_{a,b,c} (\text{amu}\text{\AA}^2)}$$

Which rotational constant(s) are completely insensitive to carbon or oxygen isotope? Why are all three constants less sensitive to carbon than to oxygen isotope (two reasons)? Hydrogen is very light and should make a small contribution to moments of inertia, yet replacement of D for H causes a very large change in one rotational constant and a negligible change in the other two.

Explain.

- H.** When you calculated rotational constants in part **G**, you probably noticed that two of the three rotational constants were almost equal to each other. Thus H_2CO is an almost symmetric top and its rotational spectrum should resemble that of a symmetric top. However, each symmetric top transition will be asymmetry-split into several resolvable transitions. In order to predict the qualitative features of the pure rotational spectrum you need to know:

- (i) Is H_2CO more nearly prolate or oblate?
- (ii) Does H_2CO have a permanent electric dipole moment and, if so, onto which principal axes can it have projections?
- (iii) What are the ΔJ and ΔK selection rules for this almost symmetric top?
- I.** Using the asymmetric top energy level expressions on page 192 of Bernath (1995 edition) (in which centrifugal distortion effects are neglected) and your predicted rotational constants from part **G**, calculate the rotational energy levels 0_{00} , 1_{10} , 1_{11} , 1_{01} , 2_{20} , 2_{21} , 2_{11} , 2_{12} , 2_{02} for $\text{H}_2^{12}\text{C}^{16}\text{O}$ and $\text{H}_2^{13}\text{C}^{16}\text{O}$. Construct an energy level diagram and draw in the transitions that would be allowed in the correct symmetric top limiting case.
- J.** Following is a complete list of observed transitions involving levels $J = 0, 1, 2$ for two isotopes

$\text{H}_2^{12}\text{C}^{16}\text{O}$	$\text{H}_2^{13}\text{C}^{16}\text{O}$
71.14 MHz	—
4829.66	4593.09 MHz
14488.65	13778.86
72837.97	71024.80
140839.54	137449.97
145602.98	141983.75
150498.36	146635.69

Assign as many of these transitions as possible. Note that, in a real spectrum, you could not arrange to see only transitions involving $J = 0, 1$ and 2 . In fact, there are more than 54 observed $\text{H}_2^{12}\text{C}^{16}\text{O}$ transitions below 150498.36 MHz.

- K.** Determine rotational constants from the observed spectra and compare with your predicted constants. Do not be alarmed that any set of A , B , or C constants cannot exactly reproduce all observed transitions. This is due to neglect of centrifugal distortion effects.
- L.** Ignoring the fact that you have measured rotational constants for the $(0, 0, 0, 0, 0, 0)$ vibrational level and not for the equilibrium molecular configuration, calculate values of r_{CH} , r_{CO} , θ_{HCH} from the observed rotational constants.