Chemistry Graduate Program
Written Qualifying Exam
Physical Chemistry
(M. Kuo, N. Kamelamela, and M.J. Shultz, *J. Phys. Chem. A* **2008**, 112, 1214-1218)
July 18, 2011

Green Chemistry Question (2 points):

1. Carbon Tetrachloride was banned in consumer products in the United States in 1970. It is very toxic and when exposed to high temperatures it can react to produce phosgene. In addition, CCl_4 has an atmospheric lifetime of 85 years and is both a greenhouse gas and an ozone-depleting agent. Briefly describe how this molecule can contribute to both global warming and the ozone hole.

Physical Chemistry Questions (10 points):

1. (2 points) Draw an isolated water molecule (or three) and identify all three axes of rotation. Which of these has the longest rotational lifetime for water caged in the carbon tetrachloride solvent, assuming that the authors conclusion of a weak interaction of the oxygen lone pair with the slightly electropositive carbon in CCl_4 is correct?

2. (2 points) The paper uses an interesting model to determine that the rotational constant about the symmetry axis for water in CCl_4 is 14.8 cm^{-1}.

    a. In general, rotational constants are used to determine what type of physical information about the molecule?

    b. Why is the rotational constant of water reduced by 2 when deuterium is substituted for hydrogen?

    c. Describe what happens to the frequency of the vibrational transitions described in this study when deuterium is substituted for hydrogen and why?

3. (2 points) Compare and contrast the experiment described in this paper (isolating a single water molecule in a solvent cage of CCl_4) with the more common molecular beam experiments used to look at small, isolated clusters of molecules.

    a. Explain how adiabatic expansion is utilized in molecular beam experiments.

4. (2 points) One of the main conclusions of this article is that the lifetime of rotation about the symmetry axis is limited due to collisions with the solvent cage.

    a. What experimental evidence do the authors present that supports this conclusion.

    b. Describe the physical origins of linewidths in the absorption and emission spectra of gases, liquids, and solids.

5. (2 points) Why does the data presented in Figure 1 differ so greatly from the FTIR spectrum of bulk water shown in Figure 2. Especially note why rotational structure is witnessed in a room temperature, liquid sample, and why there is no fine rotational structure in the spectrum.

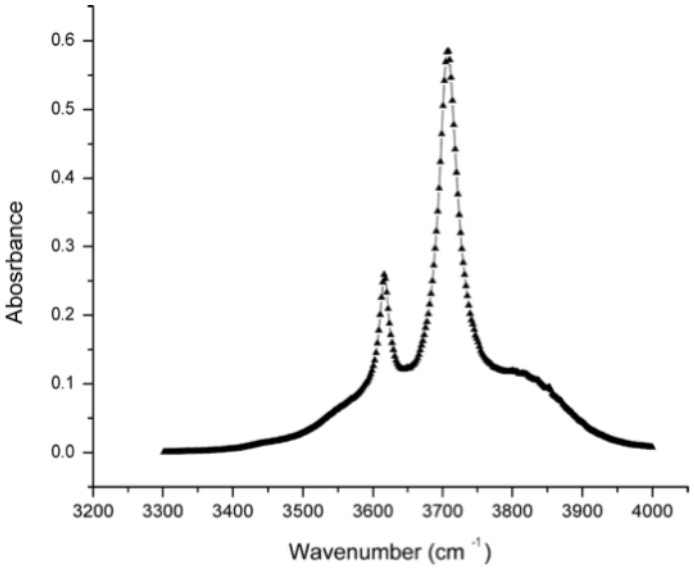

Figure 1 FTIR spectrum of water in carbon tetrachloride at room temperature. The saturated concentration is 7.5 mM.35

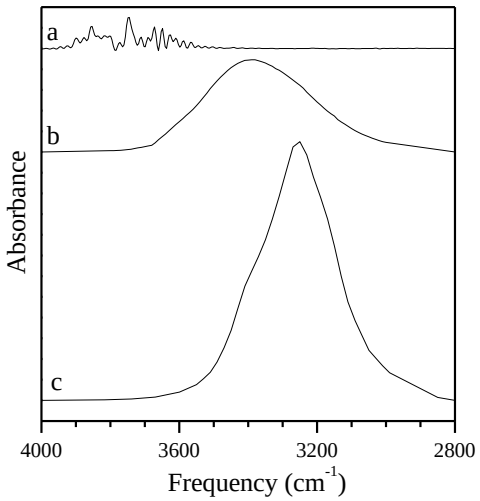

Figure 2. Infrared absorption of identical cross sections of bulk water in its three phases; a) vapor, b) liquid and c) solid.