Molecular Spectroscopy of Anthracene

Introduction

In this experiment you will explore various aspects of the molecular behavior of the polycyclic aromatic hydrocarbon (PAH) anthracene in solution using UV-visible absorption, fluorescence and IR spectroscopy to investigate the relationship between vibrations in anthracene's ground electronic state and in its first excited state. First, you will obtain the UV-visible spectrum of anthracene to define the absorption bands. The result allows you to choose an excitation wavelength with which you will obtain the fluorescence emission spectrum. Now choosing one of the fluorescence peaks, you will measure its fluorescence excitation spectrum, and ascertain its similarity to the absorption spectrum. You will also measure its IR vibrational spectrum. In analyzing the photophysical features of anthracene, the vibronic spacings of anthracene's emission versus those seen in the absorption/excitation will be compared numerically, and related to the IR spectral features. Generalized conclusions can then drawn regarding anthracene's geometry and bonding while in its excited state as compared to its ground state.

Equipment

- Shimadzu UV-2450 UV-Vis spectrophotometer & UVProbe software
- Photon Technologies Inc (PTI) fluorimeter and PC data system
- Thermo-Nicolet IR200 Fourier-transform infrared (FT-IR) spectrometer with an attenuated total reflectance (ATR) head and PC data system *or* the Shimadzu IRAffinity-1FT-IR spectrometer with IRPrestige-21 software and ATR head
- Quartz cuvettes
- Volumetric glassware

Experimental

1) Look up MSDS information of anthracene before you come to lab. Is there anything about this PAH that should concern you?
2) *Bring a flash drive to the lab with you to store your data.* If you don't have a flash drive, see your TA to borrow one.
3) Turn on the Shimadzu UV-2450 UV-Vis spectrometer to let it begin its 20 min warm up (see instructions).

4) Prepare a solution of anthracene in *n*-heptane at a concentration of ~400 µM.
5) Prepare dilutions of the 400 µM solution in heptane at 40, & 4 µM.

6) *See the instructions for using the Shimadzu UV-2450 UV-Vis spectrophotometer for details in obtaining your UV-visible absorption spectra.*

7) See the instructions for using the PTI fluorimeter for details in obtaining your UV-visible emission and excitation spectra.
   a) Determine the wavelength of one of the maxima in the absorbance spectrum, and use this as wavelength as your excitation wavelength **to obtain an *emission* spectrum of anthracene** with the fluorimeter.

b) Determine the wavelength of one of the maxima in the fluorescence spectrum, and use this as your detection wavelength **to obtain the *excitation* spectrum of anthracene**.

8) **Obtain an IR spectrum of anthracene** using the ATR head of the FT-IR spectrometer. In this part of the experiment anthracene crystals are placed on the diamond crystal of the ATR. The background subtraction is for air. (See attached guide for use of the ATR FT-IR spectrometer.)

9) Dispose of your chemical waste and clean your glassware & cuvettes:
   a) All waste is to be collected for proper disposal. The waste should be marked with as follows: *95% n-heptane & 5% anthracene*. Do not use chemical formulas.
   b) The glassware should be cleaned by rinsing with 2-3 mL of n-heptane (reagent grade) 3 times, followed by a final rinse using 1 mL of spectrophotometric grade n-heptane.
      i) NO ACETONE SHOULD BE USED ON THE GLASSWARE AT ANYTIME
      ii) If you need another solvent, try *i*-propanol

Report

Introduction:

- Discuss what the UV-vis absorption, fluorescence, and fluorescence excitation information provides you about electronic states. Relate this to the vibrational information from IR.

Results:

- Present the spectra you obtained as graphs drawn using Excel.
  - Be sure to label all of your peaks
  - Make one plot that includes both the UV-visible absorption and the fluorescence spectra
- Tabulate peak locations for each of the spectra
- Tabulate relevant IR peaks
- Identify which IR peaks correspond to which absorption, excitation or emission peak differences.

Discussion:

- Why did you choose a particular UV-vis absorption peak for obtaining the emission spectrum by fluorescence for anthracene
- What are the different types of information you obtained from the emission versus the excitation (or absorption) spectra by fluorescence for anthracene?
- Compare the energy spacings of the vibronic peaks in the absorption and excitation spectra. Are they the same or different and if different why?
- Compare the energy spacings of the vibronic peaks in the absorption and emission spectra. Are they the same or different and if different why?
- Did you observe a Stoke's shift? What it as you expected?
- Why do the intensities of the absorption peaks differ? What would you predict them to be?
- The IR peak absorptions you found should correspond to peak differences in the absorption, excitation, or emission peaks. Which do they correspond to and why?

Handouts

1. N.J. Turro, *Modern Molecular Photochemistry*, 1978, Chap 2: Electronic orbitals, configurations, and states, pp 16-37.

References

1. J.D. Ingle, Jr & S.R. Crouch, *Spectrochemical Analysis*, 1988
   a. Chap 12: Introduction to molecular spectroscopy
   b. Chap 15: Molecular luminescence spectrometry
2. D.A. Skoog, F.J. Holler & S.R. Crouch, *Principles of Instrumental Analysis*, 6th ed, 2007:
   a. Chap 6: An introduction to spectrometric methods
   b. Chap 7: Components of optical instruments
   c. Chap 13: An introduction to ultraviolet/visible molecular absorption spectrometry
   d. Chap 14: Application of ultraviolet/visible molecular absorption spectrometry
   e. Chap 15: Molecular luminescence spectrometry
3. P.W. Atkins, Chap 17: Electronic transitions, *Physical Chemistry*, 4th ed, 1990, §17.1-17.5, pp 500-512.
4. R.J. Silbey, R.A. Alberty, & M.G. Bawendi, *Physical Chemistry*, 3rd ed, 2005
   a. Chap 9: Quantum Theory
   b. Chap 11: Molecular Electronic Structure
   c. Chap 14: Electronic Spectroscopy of Molecules