**Laboratory #4a**

**Chem 6614 Instrumental Methods of Chemistry**

**SUNY Alfred State College**

***Identifying Unknown Organic Compounds via Infrared Spectroscopy***

**4.1a. Background**

You have previously used Infrared Spectroscopy (IR) in Organic Chemistry to confirm the identity of a synthesized compound. This was normally accomplished by comparing your product’s `IR fingerprint’ with the IR of a bona fide sample of the desired species in pure form. Confirmation of a successful synthesis was asserted when sufficient matches between `diagnostic’ bands of the desired organic species’ IR spectrum and that of the experimental product were found.

This straightforward approach to compound identification is adequate for organic synthesis since you know ahead of time what to look for. When a complete unknown is to be identified, however, knowing what to look for is the whole problem

Because of the advances in computer technology most IR software applications use a brute strength approach to `ID’ an unknown compound, e.g. the unknown IR is serially compared with all the IR spectra of known compounds resident in a computerized library of IR until the best matches are found . These IR search routines normally provide a list of the ten most likely identifications ranked from most to least probable and leave the choice of the `right’ compound to the analyst.

While fast and convenient computer-based IR identifications are never to be taken at face value . First, they assume that the recording conditions (and the recording instrument) of the unknown spectrum IR are identical to those assumed in the computer library and second, they often assume only one compound is present. Third and finally, the computer searches are mainly predicated on the energy positions of the various bands and give less weight to band shape and strength. It is often the case that an experienced IR user will factor in his/her intuitions and experience about these qualitative features while interpreting the IR spectrum in a way not easily mimicked by a computer program.

 A prudent analyst will thus supplement a computer-based conclusion by ‘assigning’ key features of an unknown IR using IR correlation tables to match the observed spectral features to characteristic molecular motions like a C-H stretch or a CH3-O bend.. All or most of the assignments must be consistent with the assumed molecular identity or it may be necessary to re-think the original molecular compound identification.

**4.2a. Purpose**

1. Students will be required to ***individually*** recount the basic components and `flow’ of analysis for both the traditional PE 710B dispersive IR, and the Nicolet SX 60 FTIR following instructor presentations both in lab and in lecture. (Done in class over the week. 5 pts)
2. The mid IR spectrum of a pure unknown compound will be recorded on the Spectrum 1 FTIR using the ATR head . The resident IR library will be used to provide a compund identification. The main observed bands will then assigned to their likely motions based on the computer selection . The observed bands will also be compared against published IR spectra .
3. Each student will practice preparing a blank KBr disk until an acceptably clear, continuous disk is obtained .

**4.3a. IR Design Walk-throughs**

**4.3.0a PE 710 B dispersive instrument (vintage 1970)**

The instructor will demonstrate the basic components and operating procedure for the students. While this style of instrument is no longer current, the basic features of much of an IR instrument (sans computers) are present and thus pertinent to understanding the technique.

***4.3.1a Nicolet SX 60 FTIR (vintage 1985)***

The SX-60 is one of the original commercial research FTIR originally donated to Alfred State in the mid 1990s by Kodak Inc. It is still operational –though we have retired it. Its advantage is a very accessible optical bench which facilitates both repair and instruction. (By way of comparison, the vintage 2005 instrument you will also use is much smaller and the optical bench is both harder to see and to repair.)

As with the PE710B, the instructor will demonstrate the basic components and operating procedure for the students. The basic optical pathway and principles of the SX-60 are similar to the modern PE Spectrum 1 FTIR. You will be asked to `trace’ the flow of the optical path through this instrument and explain what the various components do during the week. It is essentially the same as with the modern Spectrum 1, albeit with a much larger footprint.

**4.4.a Experimental**

**Identifying an Unknown using the ATR (Attenuated, Total Reflectance accessory) on the Perkin-Elmer Spectrum 1 (vintage 2005)**

This instrument, a gift from the U.S Drug Enforcement Agency, is a modern version of the SX 60 . Most of you have already used it during routine Organic Chemistry characterizations. As opposed to the lengthy set of keyboard commands accompanying the SX 60’s operation, the Spectrum 1 is essentially a `point and click’ instrument with a relatively intuitive command toolbar. Most, if not all of the students in your class have used it in its basic form in Organic Chemistry I.

The chief difference between the Spectrum 1 instrument and the older Nicolet SX-60, beyond size and convenience of computer control, is the former instrument’s use of an additional refinement: the ATR head. As discussed in lecture, this device allows a solid or liquid sample to be directly placed on the surface of a diamond cell through which the IR light is bounced ~ 10 times between sample and diamond surface along the plane formed by their junction. The method eliminates the need for cells, pellets, mulls and KBr disks and provides generally equivalent spectra to those obtained from these traditional sampling methods. However, the intensity of the diagnostic region is sharply reduced compared to more conventional cell-based FTIR approaches

If not already done, carry out a background scan using 10-25 scans, then repeat in Sample mode after your sample has been placed on the diamond cell face. The instructor will demonstrate the correct way to do this so that you won’t lose sample to evaporation.

If necessary, smooth your spectrum, label peaks for position, annotate your spectrum and print it.

**4.3.4a KBr pellet making**

The instructor will demonstrate the method of making a KBr pellet using the in-house pellet press and pellet die. This is a common technique for preparing solid samples for an IR scan .Each student will practice preparing a blank until a reasonably clear KBr disk is obtained, as determined by instructor inspection.

**4.4a Observations**

* Include Spectrum 1 spectra in your lab book making sure to include the conditions of the FTIR runs (e.g. scan #, cm-1 range, cell type and spacing, instrument ID, date and operator) are recorded **on** the spectra.
* Tabulate the position shape and relative intensity (vs, s, ms, m, mw, w,vw….) of **all** the significant observed peaks observed in the unknown spectrum identified in the ATR head run in a separate table

 TABLE 1

Example: **Observed band positions, shapes and intensities for unknown #1**

 **On Spectrum 1 with ATR head (Spectrum B) taken 2-5-11:**

 **4000-500 nm , 20 scan average**

 *Peak position (cm‑1) shape intensity*

 3250 broad singlet vvs

 3050 sharp doublet vvw

 2900 sharp singlet s

 2050 broad multiplet vw

 Etc…

* Use the PE IR library search and identify the top choice for your unknown and the rating % for correlation.

**4.5 a Results**

Use the IR correlation tables resident in your text (see pages 461-463 of Skoog), the Aldrich IR Atlas and the correlation table attached to this report to help verify the proposed top choice for the molecular species responsible for your spectrum suggested by the PE IR Search Library.

Once you’ve done this you should build a table like that shown in example below . It does not have to list all the peaks reported in Observations, but should represent an assignable vibrational motion pertinent to the molecular assignment. It is done to provide physical confirmation that the computer’s brute strength search results are chemically sensible. Note that the IR Search program is far from perfect and can mis-identify even easy compounds like hexane. Inclusion of published bands (from the various Atlases) along with a reference page provides further proof of identity(if-of course the observed and reference bands match)

*Example*

**RESULTS: Unknown #1 assigned to methanol, CH3OH**

***Group frequency assignment for unknown #1 as CH3OH***

***IR Correlations with group frequency motion assignments***

*1Methanol* Aldrich IR Atlas, pg A-345

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Observed ν(cm-1**)  | **Reference compound1 υ(cm-1)** | **Shape observed** | **Intensity observed** | **Molecular motion assignment** |
| **3250** | **3260** | **Broad singlet** | **vvs** | O-H stretch |
| **2900** | **2910** | **Sharp singlet**  | **S** | Symmetric C**-H stretch of** -C**H3** |
| **2820** | **2808** | **Sharp singlet** | **ms** | **Asymmetric C-H stretch of** C**H3** |
| **1410,1390** | **1400,1385** | **Broad, multiplet** | **m**  | **CH­3-O-H scissors****CH3 scissors** |
| **1025** | **1012** | **singlet** | **St** | CH3-**O**H stretch |

**Physical Rationale for identification of unknown as CH3OH.**

The strong, broad singlet at 3250 cm-1 provides clear evidence that the unknown contains an OH since such a signal is created by the O-H stretching mode. The characteristic broadness of the band reflects the role of H-bonding. Hence, an alcohol is indicated. That it is a terminal alcohol is supported by the appearance of strong singlet at 1025 cm-1, indicative of a CH3-O stretch (see correlation table below.) The absence of typical CH2 bands either at 2950 (the C-H stretch of CH2) and the absence of the scissor frequency for CH2 at 1470 means the alcohol is unusually simple and lacks any methylene groups. Thus, the IR suggests a terminal alcohol without methylenes. Since no strong, sharp, medium bands just above 3000 cm-1 appear, the alcohol is also a simple aliphatic e.g. there are no double (C=C) or triple (C≡C) bonded carbons in the structure. CH3OH is thus the most likely identity since methanol contains no methylenes and is a terminal alcohol.

The unknown bands match well those from the Aldrich IR Atlas, pg A-345 listed for Methanol selected by the PE IR search library, which rates the % certainty at 99

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Note #1: You don’t have to assign all your observed bands, but those that you do list in the final table in Results must be consistent with your molecular motion assignment

Note #2: As illustrated , you must provide a brief, written rationale below the final table arguing the merits of your assignment. Do not just list a known spectrum’s set of bands versus yours; I want an argument based on motional assignments.

Note #3: The reference band shapes and intensities may vary from the ATR results since the latter method tends to decrease the apparent absorption at high wave numbers compared to spectra taken with traditional IR cells used to record the reference spectra

**IR Correlation Table with group frequency motion assignments**

**Alkanes**

**ν (cm-1**) shape group frequency motion assignment

 **2950-2850 s doublet CH2 sym and asymmetric C-H stretch**

 **2900-2800 s doublet CH3 sym and asymmetric C-H stretch**

**1470-1430 ms ~singlet CH2 scissors**

**1360-1410 m ~singlet CH3 scissors**

710 mw br doublet ? CH3 methyl wags

**Alkenes**

**3010-3100 m singlet C=C-H vinyl C-H stretch**

**1610—1680 w singlet C=C vinyl carbon-carbon stretch**

Rest as with alkanes

**Alcohols**

**3200-3650 vs broad OH stretch**

2950-2850 s doublet CH2 sym and asymmetric C-H stretch

 2900-2800 s doublet CH3 sym and asymmetric C-H stretch

1470-1430 ms ~singlet CH2 scissors

**1400-1450 ms br ? C-O-H scissors**

**Bolded lines** are most diagnostic of given functionality

1360-1410 m ~singlet CH3 scissors

**~1020-30 vs singlet CH3**-O stretch

**Ketones**

2950-2850 s doublet CH2 sym and asymmetric C-H stretch

2900-2800 s doublet CH3 sym and asymmetric C-H stretch

**1690-1760 vs singlet C=O stretch**

1470-1430 ms ~singlet CH2 scissors

**~ 1400 ms singlet R-C(O)-R scissor ?**

1360-1390 m ~singlet CH3 scissors

**~1050-1150 mw singlet R-C=O stretch ?**

**Aromatics**

**3110-3020 ms singlet Ar-H stretch**

**1660-2000 w multiplet ring overtones(can indicate # substituents)**

**1590-1630 mw singlet(?) aromatic C=C stretches**

**1480-1520 mw singlet (?)**

**670-870 ms singlets out of plane Ar-H bends**