Raman Spectroscopy

Comparison of Raman Spectra of selected substances with Infrared Spectra obtained from the literature

Protocol (v.1.0)

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Introduction

When radiation passes through a transparent medium, the species present scatter a fraction of the beam in all directions. In 1928, the Indian physicist C.V.Raman discovered that the wavelength of a small fraction of the radiation scattered by certain molecules differ from that of the incident beam; furthermore, the shifts in wavelength depend upon the chemical structure of the molecules responsible for scattering.

The theory of Raman scattering, which now is well understood, shows that the phenomenon results from the same type of quantized vibrational changes that are associated with infrared (IR) absorption. Thus, the difference in wavelength between the incident and scattered radiation corresponds to wavelengths in the mid-infrared region. Indeed, Raman scattering spectrum and infrared spectrum for a given species often resemble one another quite closely. There are, however, enough differences between the kinds of groups that are infrared active and those that are Raman active to make the techniques complementary rather than competitive. For some problems, the infrared method is the superior tool, for others, the Raman procedure offers more useful spectra.

An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained form aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable windows. Thus aqueous solutions can be studied by Raman spectroscopy but not by IR. This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution problems. Despite these advantages, Raman spectroscopy is subject to interference by fluorescence or impurities in the sample.

In brief, a vibrational mode is IR-active when there is a change in the molecular dipole moment during the vibration; a vibrational mode is Raman active when there is a change in polarizibility during the vibration. Qualitatively, asymmetric vibrational modes and vibrations due to polar groups are more likely to exhibit prominent IR absorption, while a symmetric vibrational mode is often strong in Raman. Molecules with a center of symmetry have no fundamental lines in common in the IR and Raman spectra.

Theory of Raman Spectra

Raman spectra are obtained by irradiating a sample with a powerful laser source of visible or infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (usually perpendicularly) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001% of the intensity of the source; as a consequence, their detection and measurement are difficult. An exception to this statement is encountered with resonance Raman lines, which are considerably more intense.

Figure 1 depicts a portion of a Raman spectrum for CCl_4 excited by a laser radiation of $\lambda_0 = 488nm$ or $\bar{\nu}_0 = 20,492cm^{-1}$. The number above the peaks is the Raman shift,
$\Delta\bar{\nu} = (\bar{\nu}_S - \bar{\nu}_0)cm^{-1}$.

The scattered radiation is of three types, namely *Stokes*, *anti-Stokes*, and *Rayleigh*. The last, whose wavelength is exactly that of the excitation source, is significantly more intense than either of the two types. Three Raman peaks are found in either side of the Rayleigh peak and that the patterns of shifts on the two sides are identical. That is, *Stokes* lines are found at wavenumbers that are 218, 314, and 495cm^{-1} *smaller* than the Rayleigh peak, whereas anti-Stokes peak occur at 218, 314, and 459cm^{-1} *greater* than the wavenumber of the source. It should also be noted that additional lines can be found at ±762 and $\pm790cm^{-1}$ as well. It is important to appreciate that the magnitude of Raman shifts is independent of the wavelength of excitation. Thus, shift patterns identical to those shown would be observed for CCl_4 regardless of whether excitation was carried out with a Kr-ion laser, a He/Ne-laser, or a Nd:YAG-laser.

Fig.1 Raman Scattering;
relaxation spectrum of CCl_4

Superficially, the appearance of Raman spectral lines at lower energies relative to the excitation energy (longer wavelengths) resembles the Stokes shifts found in a fluorescence experiment (fluorescence absorption and reemission); for this reason, negative Raman shifts are called *Stokes shifts*. Shifts toward higher energies are termed *anti-Stokes*; quite generally, anti-Stokes lines are appreciably less intense that the corresponding Stokes lines. For this reason, only the Stoles part of a spectrum is generally used. Furthermore, the abscissa of the plot is often labeled simply in cm^{-1} rather than wavenumber shift $\Delta\bar{\nu}$; the negative sign is also dispensed with. It is noteworthy that fluorescence may interfere seriously with the observation of Stokes shifts but not with that of anti-Stokes shifts. With fluorescing samples, anti-Stokes signals may therefore be more useful, despite their lower intensities.
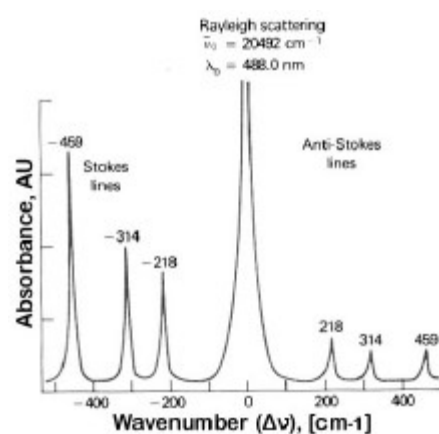
Mechanism of Raman Scattering

In Raman spectroscopy, spectral excitation is normally carried out by radiation having a wavelength that is well away from any absorption peaks of the analyte.

- The heavy arrow in figure 2 depicts the energy change in the molecule when it interacts with a photon from the source. The increase in energy is equal to the energy of the photon $h \cdot \nu$.
- The second, narrower arrow shows the type of change that would occur if the molecule encountered by the photon happened to be in the first vibrational level of the electronic ground state (at room temperature, the fraction of the molecules in this state is small).
- The middle set of arrows depicts the changes that produce Rayleigh scattering. No energy is lost in this case, as a consequence of the elastic collision between the photon and the molecule.
- The energy changes that produce Stokes and anti-Stokes emission radiation due to inelastic scattering are depicted on the right. The two differ from the Rayleigh radiation by frequencies corresponding to $\pm \Delta E$, the energy of the first vibrational level of the ground state (if the bond were to be IR-active, the energy of its absorption would also be ΔE. Thus, Raman *frequency shift* and the IR absorption *peak frequency* are identical.

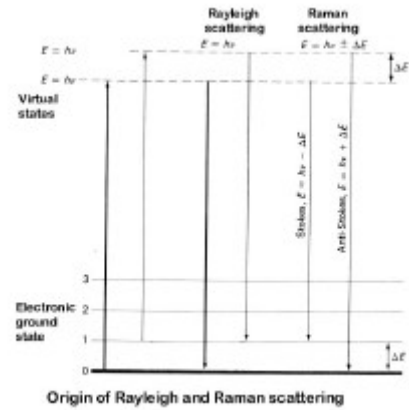
Origin of Rayleigh and Raman scattering

Fig.2 Relaxation of excited molecules and atoms

The relative populations of the two energy states are such that Stokes emission is much favored over anti-Stokes. In addition, Rayleigh scattering has considerably higher probability of occurring than does Raman scattering, because the most probable event is the energy transfer to molecules in the ground state and reemission by the return of these molecules to the ground state. Finally, it should be noted that at room temperature the anti-Stokes lines are weaker than the Stokes lines, because under these circumstances only a small fraction of the molecules are found in the first vibrationally excited state. The intensity ratio between Stokes and anti-Stokes lines is a function of temperature of the sample and will increase with temperature.

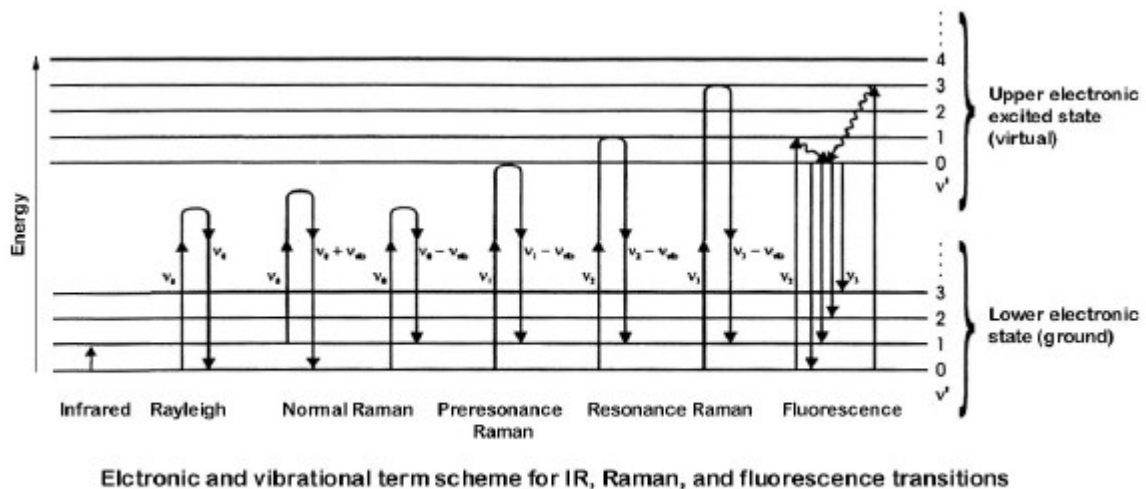Elctronic and vibrational term scheme for IR, Raman, and fluorescence transitions

Fig.3: Relaxation patterns

The regular Raman effect is very weak and can be analytically used only for the study of main components. Signal intensities can however be enhances up to $1 \cdot E^4$ times exploiting the *Resonance Raman Effect*. The enhancement is obtained by using an exciting wavelength that matches with electronic transitions of the sample (fig. 3). Both normal and resonance Raman effects maybe obscured by fluorescence, which is by a factor of $1 \cdot E^7$ more efficient than Raman scattering, when treating aromatic samples with visible or UV laser sources.

Wave Model of Raman Scattering

1. A beam of radiation having the frequency ν_{ex} is incident upon a solution of an analyte. The electric field E of this radiation can be described by the equation..

$$E = E_0 \cdot \cos(\omega \cdot t) = E_0 \cdot \cos(2 \cdot \pi \cdot \nu_{ex} \cdot t)$$

E_0, amplitude of the incident wave

2. When the electric field of the radiation interacts with an electron cloud of the analyte bond, it induces a dipole moment *m* in that bond that is given by..

$$m = \alpha \cdot E = \alpha \cdot E_0 \cdot \cos(2 \cdot \pi \cdot \nu_{ex} \cdot t)$$

α, proportionality constant of the polarizibility of the bond

3. In order to be Raman active, the polarizibility (a measure of the deformability in an electric field) of the bond must vary as a function of the distance between nuclei according to the equation...

$$\alpha = \alpha_0 + (r - r_{eq}) \cdot (\partial \alpha / \partial r)$$

α_0, polarizibility of the bond at the euqilibrium distance r_{eq}

4. The change in internuclear separation varies with the frequency of the vibration ν_v is given by ....

$$r - r_{eq} = r_m \cdot \cos(2 \cdot \pi \cdot \nu_v \cdot t)$$

r_m, maximum internuclear separation relative to the equilibrium

$$\alpha = \alpha_0 + r_m \cdot \cos(2 \cdot \pi \cdot \nu_v \cdot t) \cdot (\partial \alpha / \partial r)$$

5. Extending the equation of polarizibility with that of the internuclear separation, and by substituting the initial equation of the dipole moment, one obtains an expression for the induced dipole moment *m*,...

$$m = \alpha_0 \cdot E_0 \cdot \cos(2 \cdot \pi \cdot \nu_{ex} \cdot t) + E_0 \cdot r_m \cdot \cos(2 \cdot \pi \cdot \nu_v \cdot t) \cdot \cos(2 \cdot \pi \cdot \nu_{ex} \cdot t) \cdot (\partial \alpha / \partial r)$$

6. Recalling from trigonometry that .... and applying it to the previous equation, gives...

$$\cos x \cdot \cos y = [\cos(x+y) + \cos(x-y)]/2$$

$$m = \alpha_0 \cdot E_0 \cdot \cos(2 \cdot \pi \cdot \nu_{ex} \cdot t) +$$
$$+ (E_0/2) \cdot r_m \cdot (\partial \alpha / \partial r) \cdot \cos[2 \cdot \pi \cdot t \cdot (\nu_{ex} - \nu_v)] +$$
$$+ (E_0/2) \cdot r_m \cdot (\partial \alpha / \partial r) \cdot \cos[2 \cdot \pi \cdot t \cdot (\nu_{ex} + \nu_v)]$$

The first term of EQ 6 represents Rayleigh scattering, which occurs at the excitation frequency ν_{ex}.

The second and third terms correspond to the Stokes and anti-Stokes frequencies of $(\nu_{ex} - \nu_v)$ and $(\nu_{ex} + \nu_v)$. Here, the excitation frequency has been modulated by the vibrational frequency of the bond. It is important to note that Raman scattering *requires* that the polarizibility of a bond varies as a function of distance - that is $(\partial \alpha / \partial r)$ must be greater than zero if a Raman line is to appear.

The difference between a Raman and a IR spectrum are not surprising when it is considered that the basic mechanisms, although dependent upon the same vibrational modes, arise from processes that are mechanically different. IR absorption requires that a vibrational mode of the molecule have a change in dipole or charge distribution associated with it. Only then can radiation of the same frequency interact with the molecule and promote it to an excited vibrational state.

In contrast, scattering involves a momentary distortion of the electrons distributed around a bond in a molecule, followed by reemission of the radiation as the bond returns to its ground state. In its distorted form, the molecule is temporarily polarized; that is, it develops momentarily an induced dipole, which disappears upon relaxation and reemission.

For example, a homonuclear molecule such as nitrogen (N_2), chlorine(Cl_2), or hydrogen (H_2) has no dipole moment either in its equilibrium position or when a stretching vibration causes a change in the distance between the two nuclei. Thus, absorption of radiation at this vibrational frequency cannot occur. On the other hand, the polarizibility of the bond between the two atoms of such a molecule varies periodically in phase with the stretching vibrations, reaching a maximum at the greatest separation and a minimum at the closest approach. As a consequence, a Raman line shifted by the amount corresponding in frequency to that of the vibrational mode results (see above, EQ 6).

Raman activities for carbon dioxide for example, show no change in dipole in the symmetric vibrational mode, as the two oxygen atoms move away from or toward the central carbon atom; thus, this mode is IR inactive. The polarizibility, however, fluctuates in phase with the vibration, because distortion of bonds becomes easier as they lengthen and more difficult as they shorten. Raman activity is associated with this mode.

In contrast, the dipole moment of carbon dioxide fluctuates in phase with the asymmetric vibrational mode. Thus, an IR absoroption peak arises from this mode. On the other hand, while the polarizibility of one of the bonds increases as it lengthens, the polarizibility of the other decreases. Thus, the asymmetric stretching vibration is Raman inactive.

Methods

Liquid State Raman Spectroscopy: Accurate examination of **liquid** samples can be performed with a complex array of optical instruments that use laser light and a high resolution detecting device. The instrumentation for modern Raman spectroscopy consists of three major components (fig.4):

- **Light / excitation source**: The Ar^+-laser used operates in a continuos mode at an initial power output of approx. 475mW with an emission wavelength of 514.531nm.

  In this special application the laser source used for Raman scattering is also used in a second similar experiment (not of interest for this purpose). Therefore, a beam splitter, set of optical mirrors, iris, polarizer, are used to diverge the laser light into the sample compartment. Sample handling for Raman studies is simpler than for IR spectroscopy because glass can be employed for windows, lenses, and other optical components instead of the more fragile and atmospherically less stable crystalline halides.

- **Raman Spectrometer**: A computerized double-beam spectrometer is used. Automation makes sure that the software positions the grating (via a step-motor) into the proper position; i.e. being a precise tool, the machine does not detect the entire spectrum at once, but rather limits the wavelength window to a certain sub-spectrum.

  Furthermore it is essential to run a blank scan in order to detect the noise level of the entire setup (it will be subtracted from each sample scan to obtain real values).

  In order to suppress extra noise and to obtain sufficiently accurate results, a wide range CCD-camera, cooled with liquid N_2 is used as the detecting device (a photo-multiplier would even enable the investigation of the weaker anti-Stokes lines).

  The discrete instrumentation used requires calibration prior to scanning the samples of interest.

Fig.4 **Instrumentation used in monochromatic Raman spectroscopy**

1, laser (hidden behind photo spectrometer);
2, beam splitter;
3, iris;
4, polarizer and rotor;
5, sample compartment;
6, analyzer and double spectrometer;
7, CCD-camera (not shown - sits on top of photo-spectrometer);

To lower the operating temperature of the CCD camera, it is necessary to fill its cooling compartment with liquid nitrogen several hours before experimentation.

Note: use protective gloves and eyewear when accomplishing this task!

After a 15 to 30min warming-up phase of the laser source, the entire beam deflection system requires proper alignment to yield best results. Upon starting the computerized photo-spectrometer (SPCTMAX), a CCl_4 sample is placed into the sample compartment, and the program parameters set to repetitive scanning (continuous acquisition) mode. To make sure that the laser is pointed properly of the sample, the following adjustments are required (both procedures result in maximal amplitudes of Stokes lines in the readout of the CCD-detecting device).

- The beam splitter is positioned in a way that the laser light is centered properly through the opening of the prepositioned iris;
- as the polarized laser light somewhat randomized as it is routed via the mirrors and beam-splitters in place, the polarization plane has to be shifted back to the V-plane; this is done by orienting the polarizer into the proper 90° position
- doing so not only suppresses Rayleigh in favor of Raman scattering, but enables the investigation of both vertical (VV) and horizontal (HV) plane-polarized light scattering to be analyzed by the double-beam spectrometer.
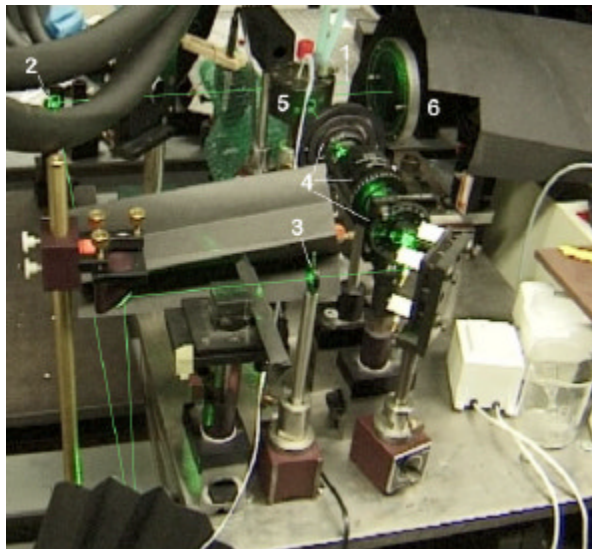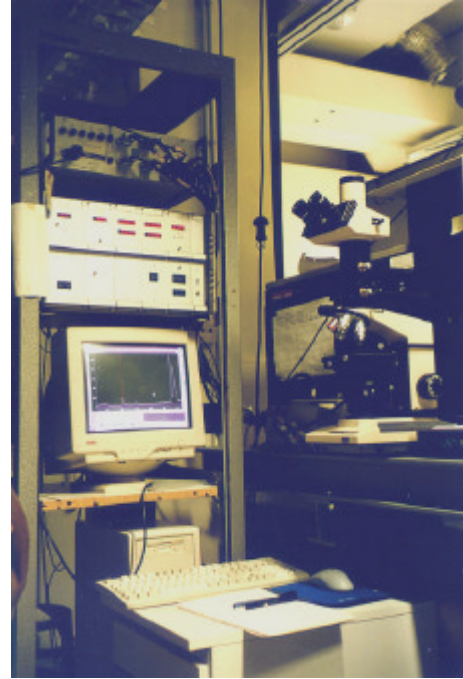
Solid State Raman Spectroscopy:

Accurate examination of **solid** samples can be performed with the same setting.

The only adaptations required involve a sample holding compartment where the laser beam is deflected through a microscope (top illumination microscope – fig.5). The sample itself is pressed into a tiny sample cup that can be easily fitted into the object holder of the microscope.

In addition to the adjustment procedure described in the previous page, the solid sample is brought into focus by using a pilot lamp in the visible spectrum.

Once in focus, the laser beam is routed through the optical system of the microscope. To avoid vaporization of the sample by excessive laser light power, and subsequently unwanted coating of the microscopes objective-lens, several preliminary trials should be run by placing a sequence of absorbing gray filters (10% gray filters) into the light path. Trials with gradually decreasing optical density (net increase in laser light power) should be used first while examining Raman peak intensity on the display as well as visual verification with the pilot lamp after each trial until the maximal Raman peak intensity is reached prior to vaporization.

Fig. 5 Instrumentation for Solid State monochromatic Raman Spectroscopy

Alternative Method:

An alternative method based on interferograms, that yields spectra much faster than the previous method is the Fourier-Transform Raman Spectroscopy (FT-RS). Both solid, liquid, and in special cases even gasoues samples can be screened with this device. The FT Raman Spectrometers is based on the Michelson interferometer principle and can be operated with one single beamsplitter for the whole spectral area of interest (4000-10cm^{-1}). This is possible because the exciting Nd:YAG laser emits around 10000cm^{-1} frequency range (1.06µm = near IR) and the Raman shift effect produces vibrational shifts of 4000cm^{-1} at most) away from this exciting line. This interval is, however, well within the range of transparency of the beamsplitter. Besides the laser source and the special detector, the only modification necessary for the adaptation is an efficient filter to eliminate the strong Rayleigh line, which would otherwise completely obscure the FT-Raman spectrum.

Fig. 6 Interferogram or
FT-Raman Spectroscopic device:

1, PC (not shown)
2, CRT display
3, Microscope
4, Laser tube
5, Probe holder w/ fine screws for focusing
6, Power control unit proper adjustment of laser intensity
7, Photomultiplier w/ CCD-camera

Conversion from wavelength to wavenumber and vice versa:

With the given laser source (emission wavelength 514.308nm), the wavenumber can be calculated as:

$$\bar{v} = \frac{1}{\lambda_{Laser}\ [nm]} \cdot \frac{1 \cdot E^7\ [nm]}{[cm]} = \frac{1}{514.308} \cdot 1 \cdot E^7 = 19444 cm^{-1}$$

Rayleigh scattering at this particular excitation frequency occurs at 19.444E^3 cm^{-1}; by convention, the excitation frequency is assigned the reference wavenumber "0". If stoke shifts in Raman scattering are observed for example at 3000cm^{-1}, the corresponding wavelength is obtained by rearranging the above formula:

$$\lambda_{RS} = \frac{1}{v_{laser} - v_{RS}\ [cm^{-1}]} \cdot \frac{1 \cdot E^7\ [nm]}{[cm]} = \frac{1}{19444-3000} \cdot 1 \cdot E^7 = 608.12 nm$$

i.e.: incident radiation (blue-green) results in a stokes re-emission spectrum that is orange in color.

Experimentation with the discrete Raman Spectroscope

Choosing the appropriate scanning samples is based upon the reference IR spectra provided by the lecturer. In our case the samples chosen have been made in accordance with the software-package "IR-TUTOR" issued by the University of San Diego. Based on this demonstration program, the following samples have been chosen for further examination in Raman spectroscopy: **n-hexane**, **cyclo-hexane**, **tuolene**, and **benzene**. **β-carotene**

Preparation: To avoid any contamination which could lead to fluorescence, and falsification of the final results, all the equipment used to extract and fill the sample containers have to be cleaned and rinsed properly with acetone and dried using an appropriate aspiration tool.

Approximately 5mL of each test solution are pipetted into separate sealable sample containers.

Note: Benzene is known to be cancerogenous; besides using gloves, handling of this substance should be done under an aspirator.

Each substance demonstrated in the IR-TUTOR software highlights distinct bands of vibrational and rotational transitions within the overall spectrum. Since the entire machinery used in this experimentation is only capable of handling a narrow spectrum at a time, we were forced to focus onto the distinct sub-spectra as indicated by the IR-TUTOR.

Practical: Prior to any measurements, an alignment procedure should be performed. Placing a Xe-lamp with a known emission wavelength (e.g. 1750cm^{-1}) in front of the double-beam spectrometer enables calibration of the detection device. Furthermore, some parameters of the SPCTMAX-software have to be set properly; clicking onto the *CCD-setup* icon of the main page opens the general CCD settings menu. According to the data table given below, each substance is scanned with the associated parameters. These parameters guarantee that each scan will be executed in a way that utilizes the maximal readout range provided by the hardware (to exit the CCD-settings page, confirm with *OK*).

By now the sample should be place into the sample compartment. Before starting a measuring cycle, the current file requires proper naming; this is done by clicking onto the *ACQUIRE* button; finally, the return key triggers the internal hardware to move the step-motor into the preset position which initiates the recording of the sub-spectrum according to the specified center frequency (ν_{center}).

Data table:

Substance	1st ν_{center} [cm^{-1}]	2nd ν_{center} [cm^{-1}]	3rd ν_{center} [cm^{-1}]	4th ν_{center} [cm^{-1}]	5th ν_{center} [cm^{-1}]	Integration time[1]) [sec]	Accumulation[1]) [-]
n-hexane	700	1375	1455	2875	2925	10	3
cyclo-hexane	700	1375	1455	2875	2925	5	3
toulene	720	1475	1600	2900	3030	5	3
benzene	720	1475	1600	2900	3030	5	3
β-carotene							
Fluorescine[2])	700	1375	1455	2875	2925	10	3
CCl$_4$ [3])	400	-	-	-	-	5	1

([1]) associated parameters that have been determined by trial and error;

([2]) Correction of instrumentation error: The hardware used is known to produce certain artifacts. The major two errors which require correction were found to be non-linearity, and declining sensitivities at the edges of each sub-spectrum.

For correction, each sub-spectrum needs to be scanned with a fluorescing reference sample (fluorescine); although it is not known whether this substance fluoresces evenly throughout the entire spectra, it has been used anyway because a polychromatic light source with constant intensities throughout the spectrum was not available. In addition, a single fluorescine sub-spectra is considered to be linear as the width of each sub-spectra is quite narrow, hence resulting in a negligible error.

([3]) CCl$_4$ is used as a calibration substance to adjust the polarizer's angle in order to maximize Raman peaks in the appropriate polarization plane to obtain VV and HV spectra.
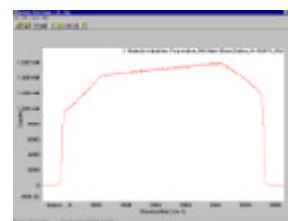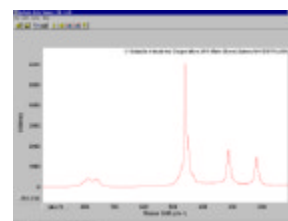

Fig 6a Reference sub-spectrum of fluorescine

Fig.6b Raman scattering of CCl$_4$ adjustment peaks

Data conversion:

The data obtained require further processing. The GRAMS-software package supplied by GALACTIC enterprises is capable of correcting instrumentation related errors, thus enabling a final evaluation of the gathered information. After importing each file into this software package, correction of each sub-spectrum is possible by a series of mathematical algorithms (cyclo-hexane of the 2950cm^{-1} and 2875cm^{-1} sub-spectra are used to demonstrate data conversion):

Compensation of non-linearity:

1. superimpose both the sample sub-spectrum and the reference spectrum associated to this particular ν_{center} (Fig 7a – 7d);
2. place the cursor onto the largest peak of the sub-spectrum and create an auxiliary ordinate that crosses the reference spectrum; record the numerical value of the cross-point provided by the lateral display;
3. enter the arithmetic function sub-menu and multiply the sub-spectrum with the numerical value obtained previously (= constant), and add the product graph into the display window;
4. again, swap to the arithmetic function sub-menu and divide the product graph by the reference spectrum; do so by defining the following:
   new term file = fluorescence spectrum
   operand = new term file with *k = 1*
   (Fig 7e and 7f)
   activate *replace previous* math function
5. clip edges that contain irrelevant data by using the *truncate* icon within the arithmetic function sub-menu;
6. and save the modified sub-spectrum (Fig 7g and 7h);

Merging adjacent sub-spectra to obtain a single continuos spectrum:

If two neighboring sub-spectra should be merged to yield a continuos single sub-spectrum, the procedure outlined above has to be executed involving both sub-spectra and their associated reference spectra.

7. superimpose both the two sample sub-spectra and the two associated reference spectra;
8. place the cursor onto the cross-point of the two reference spectra and record the numerical value provided by the lateral display;
9. perform step three to six of the above recipe; ....
10. load both sub-spectra (Fig 7g and 7h) into one file by superimposing one with the other;
11. there is a chance that the merged sub-spectra differ slightly in the allover amplitude yielding a double image; to create a single graphical display, calculate the arithmetic average by using the arithmetic function sub-menu;
12. and save the final sub-spectrum (Fig 7i);

Fig 7a fluo reference sub spectrum ν_{center} 2925cm^{-1}

Fig 7b fluo1 reference sub spectrum ν_{center} 2875cm^{-1}

Fig 7c c-xvv1 sub-spectrum as obtained from spectrometer

Fig 7d c-xvv sub spectrum as obtained from spectrometer
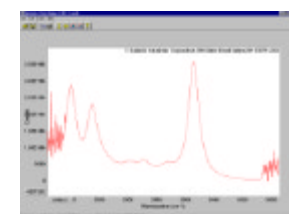

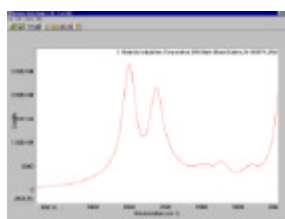Fig 7e c-xvv1k corrected sub spec.

Fig 7f c-xvvk1 corrected sub spec.

Fig 7g c-vv1kk truncated raw sub spec.

Fig 7h c-vckk trncated raw sub spec.

Fig 7i c-xvvkks; merged sub-spectra of the respective ν_{center} 2925cm^{-1} (left) and ν_{center} 2875cm^{-1} (right)
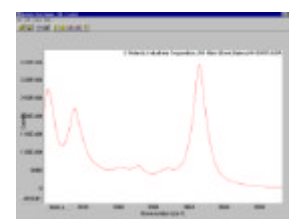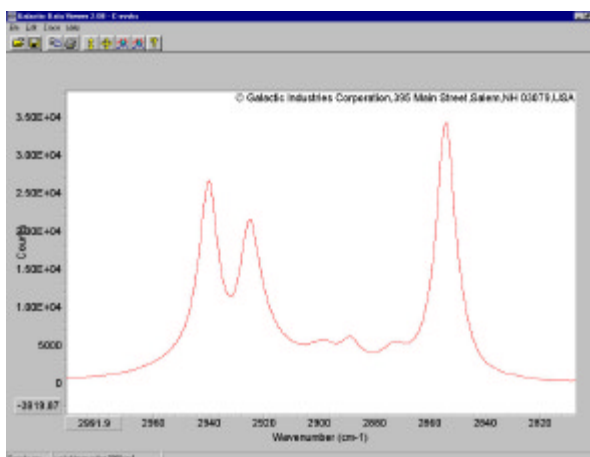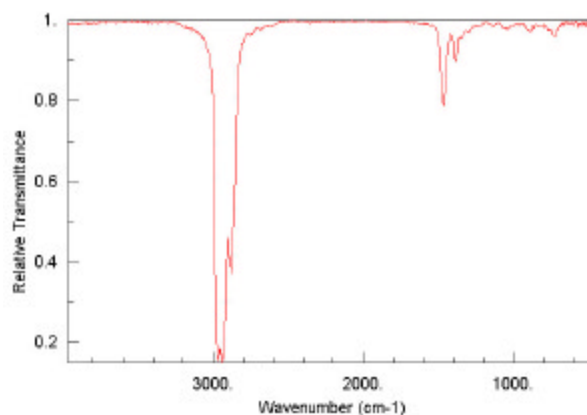
Results

n-hexane

Fig 8. IR-Spectrum of hexane
(according to *NIST Chemistry Webbook*)

Raman Sub-Spectra of n-hexane:

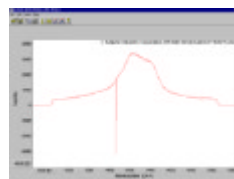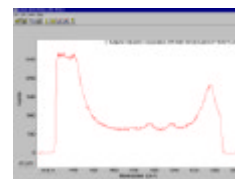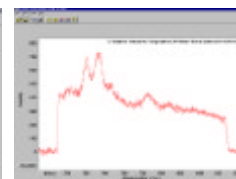Fig.8a n-hvv1   Fig.8b n-hvv   Fig.8c n-h2vv   Fig.8d n-h3vv   Fig.8e n-h4vv

Discussion (n-hexane):

Chemical properties: N-hexane is a colorless liquid with a slightly disagreeable odor with the chemical formula C_6H_{14} [structural formula $CH_3(CH_2)_4CH_3$]. It evaporates very easily into the air and dissolves only slightly in water. It is highly flammable, and its vapors can be explosive. It may be ignited by heat, sparks, and flames. N-hexane can react vigorously with oxidizing materials such as liquid chlorine, concentrated oxygen, and sodium hypochlorite. It will attack some forms of plastics, rubber, and coatings. It is insoluble in water and miscible with alcohol, chloroform, and ether. Synonyms for n-hexane are hexane and hexyl hydride.

Fig.8f chemical structure

Spectrum Interpretation: The CH_3 asymmetrical and symmetrical stretchings occur near 2962 and 2872cm^{-1}, respectively. The intensities of these vibrations are strong, and their frequencies are characteristic. The asymmetric and symmetric CH_3 bendings occur at 1470-1430cm^{-1}. The asymmetric bend band near the 1460cm^{-1} has a medium intensity in both IR and Raman spectra, while the CH_3 symmetric bend near 1380cm^{-1} is medium in the IR but is very weak in the Raman. The asymmetric and symmetric CH_2 stretchings appear strongly at about 2926 and 2853cm^{-1} in IR and Raman. Again, the spectral positions vary no more than $\pm10cm^{-1}$ for acylic $-CH_2-$ groups. The four bending vibrations of CH_2 groups are scissoring, rocking, wagging, and twisting. The scissoring mode of the CH_2 group gives rise to a characteristic band near 1465cm^{-1} in IR and Raman spectra. This band often overlaps with CH_3 asymmetrical bending. These vibrations are affected by interaction with neighboring CH_2 groups and give rise to weak IR and medium Raman bands for alkanes.

The structure of hexane can be viewed at:

http://www.recipnet.indiana.edu/common/Simple_stuff/hexane/hexane.htm

Cyclo-hexane

Fig.9 IR-spectrum of cyclo-hexane
(according to *NIST Chemistry Webbook*)
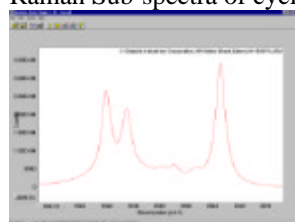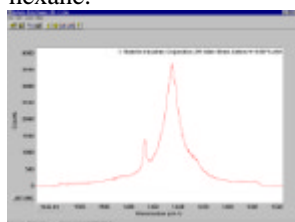
Raman Sub-spectra of cyclo-hexane:
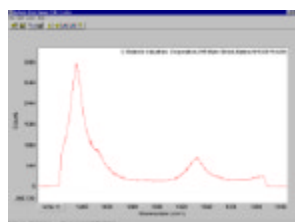

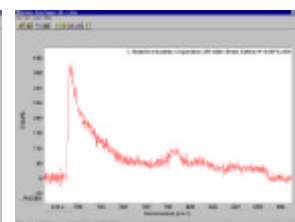| Fig.9a curvefit | Fig.9b c-x2vv | Fig.9b c-x3vv | Fig.9d c-x4vv |

Discussion:

Chemical properties: Cyclohexane, colorless, volatile liquid C_6H_{12}, with a pungent odor, produced by the hydrogenation of benzene and the distillation of petroleum. It is used primarily as a solvent for paints, resins, varnish, and oils and as an intermediate in the manufacture of other industrial chemicals and nylon fibers. Cyclohexane freezes at 6.55° C and boils at 80.74° C.

Fig.9e chemical structure

Spectrum Interpretation: The CH_2 asymmetrical and symmetrical vibrational modes in the 2933-2915cm^{-1} and 2897-2852cm^{-1} regions are very strong in Raman and IR spectra. The CH_2 scissoring is located at 1450cm^{-1} for cyclohexane. The CH_2 strectching and bending frequencies occur in the dame regions as those found for open chain alkanes.

The skeletal vibrations are prominent in the region below 1100cm^{-1}. For cyclohexane, the strong IR band at 903cm^{-1} can be assigned to an asymmetric stretching mode. In chair-form cyclohexane, a strong ring breathing mode at 802cm^{-1} was observed.

The *cis* and *trans* isomers of dialkyl cylcohexanes can be distinguished by their characteristic Raman frequencies below 1000cm^{-1}.

An FT-Raman scan can of cyclohexane be viewed at:

http://chemistry.mps.ohio-state.edu/~rmccreer/freqcorr/images/cyclo.html
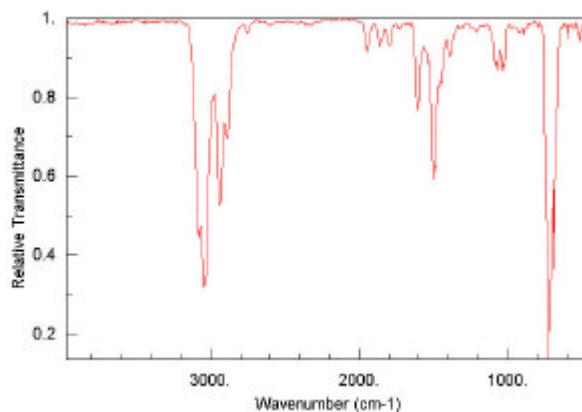
The structure of cyclohexane can be viewed at:

http://www.recipnet.indiana.edu/common/Simple_stuff/cyclohexane/cyclohexane.htm

Toulene

Fig.10 IR-spectrum of toulene
(according to *NIST Chemistry Webbook*)
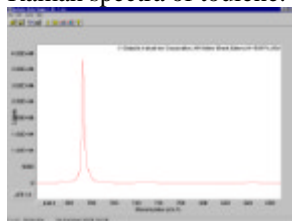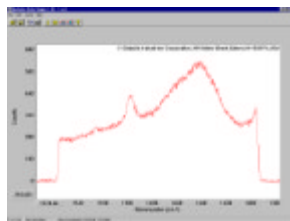
Raman spectra of toulene:
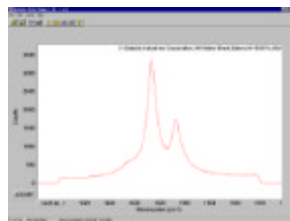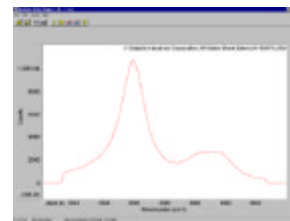

Fig.10a T-vv

Fig.10b T-vv1

Fig.10c T-vv2

Fig.10d T-vv3

Discussion:

Chemical properties: Toluene, colorless hydrocarbon with the chemical formula C_7H_8 (structural formula $C_6H_5CH_3$). It occurs in coal tar, specific gravity 0.86, boiling point 110.6°C. The name toluene reflects the way in which it was once prepared, through destructive distillation of balsam of tolu. A great deal of industrial toluene is prepared in oil refineries by the alkylation of benzene. It is used as a solvent and as a source of synthetic compounds, for example, in the production of trinitrotoluene. Prolonged breathing of toluene vapor is harmful and should be avoided. Synonyms for toluene are phenyl methane, methyl benzol methylbenzene, toluol, and methyl benzene.
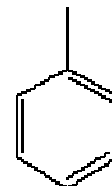

Fig.10e
chemical
structure

Spectrum Interpretation: The R_3C-H stretching mode absorbs near $2890cm^{-1}$. This band is found in a broader region ($3000-2850cm^{-1}$) when the CH is adjacent to a non-carbon atom. This band is weak, and its presence is often obscured by the much stronger CH_3 and CH_2 stretching bands in both IR and Raman spectra. The tertiary C-H bending usually occurs near $1360-1359cm^{-1}$ but is not visible in toulen in both IR and Raman spectra.
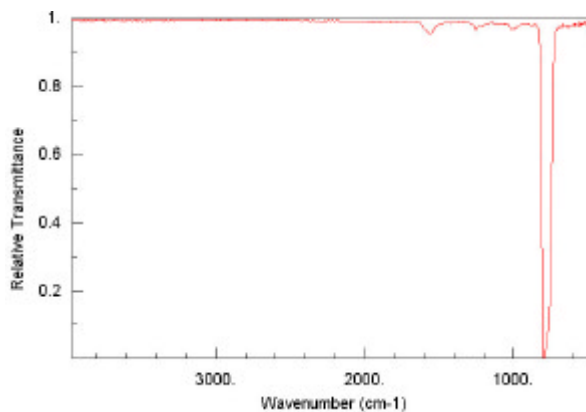
The CH_3 asymmetrical and symmetrical stretchings occur near 2962 and $2872cm^{-1}$, respectively. The asymmetric and symmetric CH_3 bendings occur at $1470-1430cm^{-1}$. The asymmetric bend band near the $1460cm^{-1}$ has a medium intensity in both IR and Raman spectra, while the CH_3 symmetric bend near $1380cm^{-1}$ is medium in the IR but is very weak in the Raman Unfortunately the Raman spectrum at this particular frequency range has not been performed, thus cannot be confirmed. The asymmetric and symmetric CH_2 stretchings appear strongly at about 2926 and around $2853cm^{-1}$ in IR and to a lesser extent in Raman. Again, the spectral positions vary no more than $\pm10cm^{-1}$ for acylic $-CH_2-$ groups. The four bending vibrations of CH_2 groups are scissoring, rocking, wagging, and twisting. The scissoring mode of the CH_2 group gives rise to a characteristic band near $1465cm^{-1}$ in IR and Raman spectra. Again, this band often overlaps with CH_3 asymmetrical bending.

An FT-Raman scan can of toulene be viewed at:

http://chemistry.ohio-state.edu/~rmccreer/freqcorr/images/toluene.html

Carbon-tetrachloride

Fig.12 IR-spectrum of carbon-tetrachloride
(according to *NIST Chemistry Webbook*)
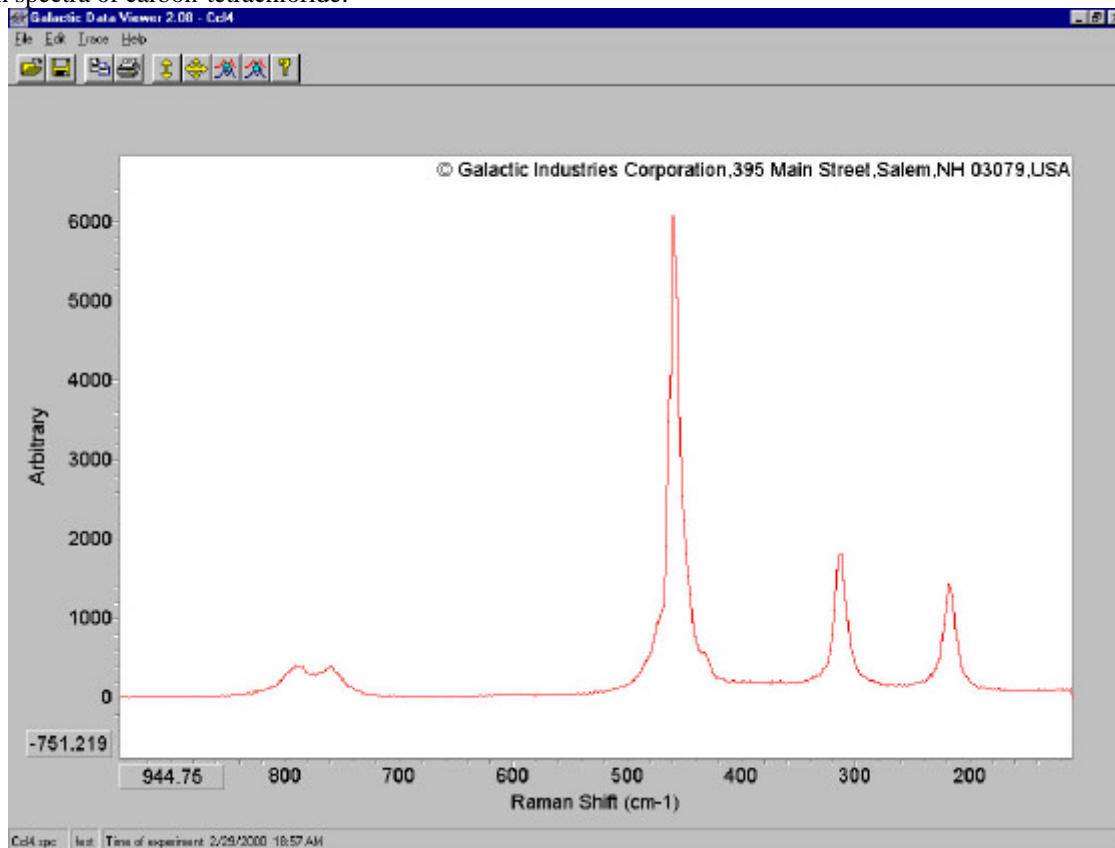
Raman spectra of carbon-tetrachloride:

Fig.11a FT-Raman spectrogram of carbon-tetrachloride

Discussion:

The FT-Raman spectrogram has been recorded by running 50 cycles with the FT-instrument.

Chemical properties: It is a heavy, colorless liquid, and has a characteristic nonirritating odor. Chemical formula CCl_4. It has a freezing point of -22.92°C, a boiling point of 76.72°C, and a density of 1.5947 g/ml at 20°C. It is made by treating carbon disulfide, CS_2, with chlorine, Cl_2, or sulfur monochloride, S_2Cl_2, or by the chlorination of hydrocarbons. Carbon tetrachloride is used to make compounds such as chlorofluoromethanes, used as refrigerants and aerosol-spray propellants. Carbon tetrachloride is also used in fire extinguishers and for dry cleaning of fabrics. Other Names: Methane, tetrachloro-; benzinoform; Carbon chloride (CCl_4).

Fig.11b chemical structure

Spectrum Interpretation: The IR-spectrum yields a group of peaks associated to the 4 chloride atoms that range in the 840-740cm^{-1} for the asymmetric stretching and 730-660cm^{-1} for the symmetric vibrations. Another symmetric vibration is found with 325cm^{-1} characteristic. A distinct C-Cl stretching frequency is found around the 460cm^{-1} band that is more or less spread according to the Cl-isotopes present in the molecules.
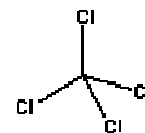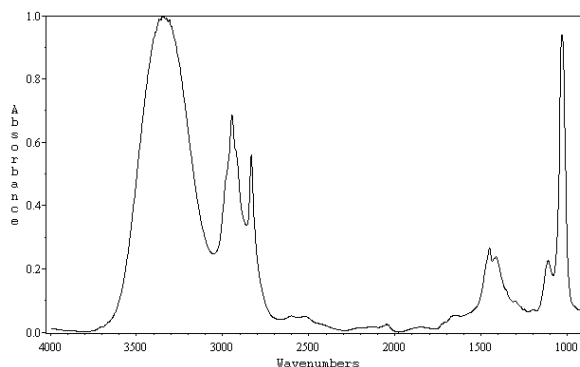
Methanol

Fig.12 IR-spectrum of methanol
(according to *DS-FTIR library*)
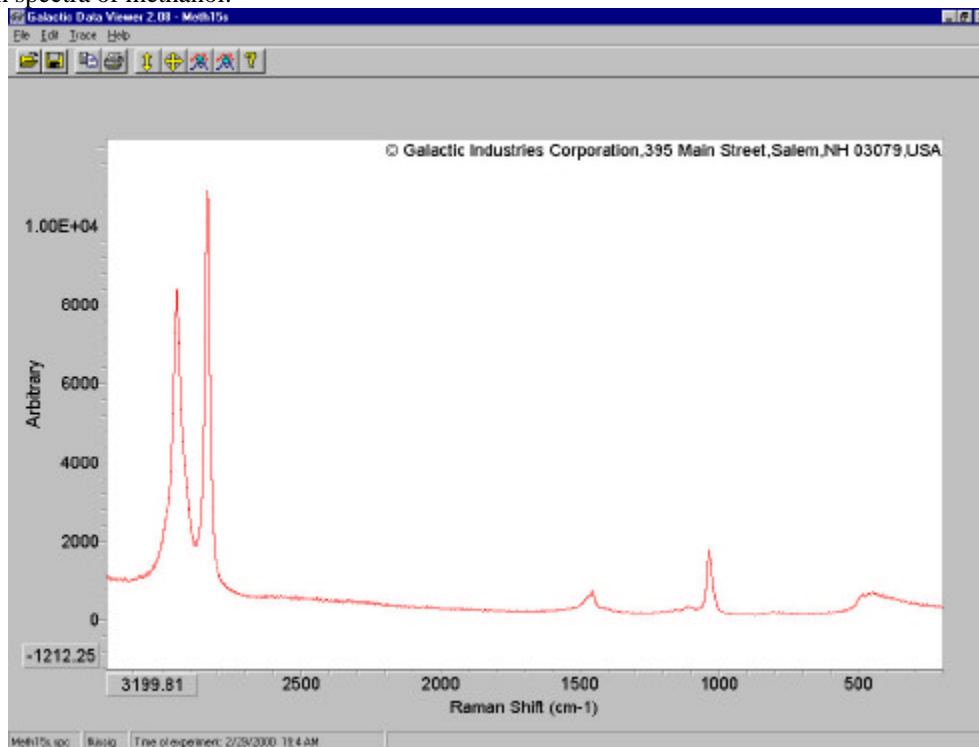
Raman spectra of methanol:

Fig.12a FT-Raman spectrogram of methanol

Discussion:

Chemical properties: Methyl alcohol, or methanol, CH_3OH, is the simplest of all the alcohols. It was formerly made by the destructive distillation of wood; however, almost all of the methanol produced today is synthetic, made from hydrogen and carbon monoxide. Methanol is used as a denaturant for grain alcohol, as an antifreeze, as a solvent for gums and lacquers, and in the synthesis of many organic compounds, particularly formaldehyde. When taken internally, by either drinking the liquid or inhaling the vapors, methanol is extremely poisonous. Methanol melts at -97.8°C, boils at 64.7°C, and has a specific gravity of 0.7915g/ml at 20°C. Other Names: Methanol; Carbinol; Methyl hydroxide; Methylol; Monohydroxy-methane; Wood alcohol; Colonial spirit.
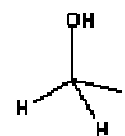
Fig.12b chemical structure

Spectrum Interpretation: Since the O-H stretching shows very weak scattering in the Raman spectrum, only the characteristic IR absorption could be emphasized. It would be a characteristic band that is located above the $3600cm^{-1}$ band.

The asymmetric and symmetric CH_3 bendings occur at $1470-1430cm^{-1}$. The asymmetric umbrella bend band near the $1460cm^{-1}$ has a medium intensity in Raman spectra (would be visible in (in both IR as well), while the CH_3 symmetric umbrella bend near $1380cm^{-1}$ is medium in the IR and very weak in the Raman. The CH_3 asymmetrical and symmetrical stretchings occur near 2962 and $2872cm^{-1}$, respectively.

β-carotene (Unfortunately, no IR-image was available for comparison)

Raman Sub-spectra of β-carotene (monochromatic scan) of carotene dissolved in carbon-tetrachloride:
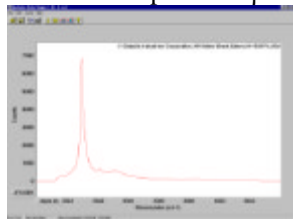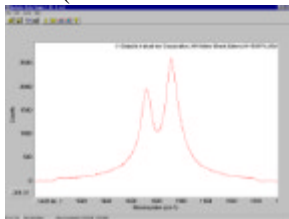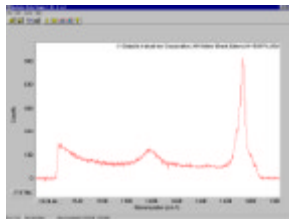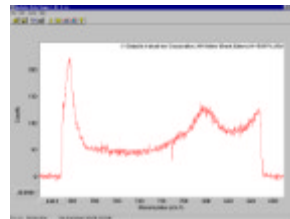

Fig 13a b-vv3

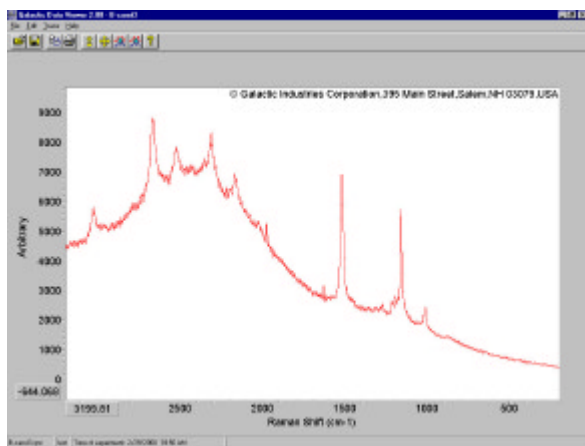Fig 13b b-vv2

Fig 13c b-vv1

Fig 13d b-vv

Fig 13e b-carot
FT-Resonance Raman spectrum of solid β-carotene
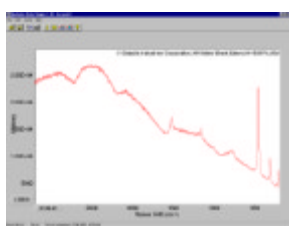

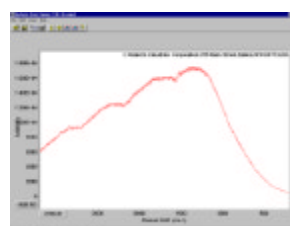Fig 13f b-carccl4
β-carotene in CCL₄

Fig 13g b-carmet
β-carotene in methanol

Resonance Raman spectrograms of solid samples are obtained by using a stimulating wavelength that is close or matches with the absorption wavelength of carotene (514,7nm = blue-green or a in wavenumbers: ≈750cm^{-1}); working with this frequency requires low-powered laser, otherwise the substance will evaporate and ultimately condense onto the microscope's object lens.

Discussion: (β-carotene): Carotene was analyzed both with the discrete Raman spectroscope as well as with the FT-Raman spectroscope. For the discrete Raman
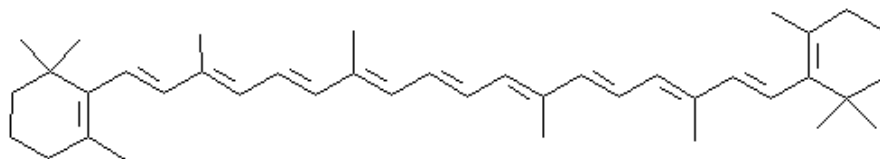

Fig.13k chemical structure of carotene

spectrogram, both a solid sample (pure carotene – fig,11a-d) as well as *dissolved* carotene (in either methanol – fig.13f or CCl₄ –fig.g13c) were screened. As observable from the scans, carbon-tetrachloride is a much better solvent for carotene than methanol, as it interferes less with the vibrating spectra of the analyte. Only the pure sample from the FT-Raman spectroscope provided a continuos spectrum of the solid sample.

Chemical properties: Beta-carotene, Retinol ($C_{40}H_{56}$) or vitamin A as it is also known is an essential light-sensitive molecule. Upon photonic bombardment, it switches from the *cis-* to the *trans* confirmation. In plants, this macromolecule is one of the many crucial proteins that are held responsible for efficient photosynthetic activity besides signing responsible for the reddish to orange hue during the fall's season.

Spectrum Interpretation: The C=C stretching frequency of ethylene occurs in the neighborhood of 1650cm^{-1} and is very characteristic for this type of substitution. The strong, highly polarized nature of this vibrational mode makes it a very useful Raman band. The C=C stretching frequencies are seen at 1623cm^{-1} and 1645cm^{-1} respectively. The characteristic IR bands in the 681-610cm^{-1} region are attributed to the C-H bending modes. For monoalkyl acetylenes, these vibrational modes occur in a narrower region of 640-628cm^{-1}. The intensity is usually very strong in IR, while it is median to weak in Raman.
The C-C stretching bands (1161-758cm^{-1}) are weak in IR and not simple characteristic frequencies in Raman. The identification of these vibrational bands is more difficult because other types of C-C stretching vibrations also occur in the same region (around 1300cm^{-1}) and can interact with each other.
The R_3C-H stretching mode absorbs near 2890cm^{-1}. This band is found in a broader region (3000-2850cm^{-1}) when the CH is adjacent to a non-carbon atom. The CH_3 asymmetrical stretching occurs near 2962cm^{-1}. The asymmetric and symmetric CH_3 bendings occur at 1470-1430cm^{-1}. The asymmetric bend band near the 1460cm^{-1} has a medium intensity in both IR and Raman spectra, while the CH_3 symmetric bend near 1380cm^{-1} is medium in the IR but is very weak in the Raman.

References:

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- D.A. Skoog, J.J.Leary; 1992 *Instrumental Analysis* 4th ed., Saunders College Publ.; Florida – USA
- Lin-Vien D., Colthup N.B., Fately W.G., Grasselli J.G. 1991; The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press Inc., San Diego - USA
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- *Pelletier M*.J., 1999; Analytical Applications of Raman Spectroscopy; Blackwell Science; London - UK

Related sites on the WWW:

- Tutorial of spectroscopy
  http://www-wilson.ucsd.edu/education/spectroscopy/spectroscopy.html
- Galactic Data Viewer
  http://galactic.com/products/dataviewer/download.asp
  http://spectra.galactic.com/SpectraOnline/code/CmpdForm.asp
- Raman Group web page
  http://www.ictp.csie.es/ramanft/eraman.html
- World Wide Web sites on Raman spectroscopy
  http://www.chem.ucl.ac.uk/resources/raman/speclib.html
- The internet journal of vibrational spectroscopy
  http://www.ijvs.com/
- Chemistry Explorer
  http://www.iversonsoftware.com/reference/chemistry/
- Safety Health and the Environment
  http://www.crossroads.nsc.org/chemicals.cfm
- Woordenboek Organische Chemie
  http://www.sci.kun.nl/woc/gui/start_en.html
- National Institute of Standards and Technology
  http://webbook.nist.gov/chemistry/
- David Sullivan FT-IR Library
  http://www.che.utexas.edu/~dls/ir/ir_dir.html