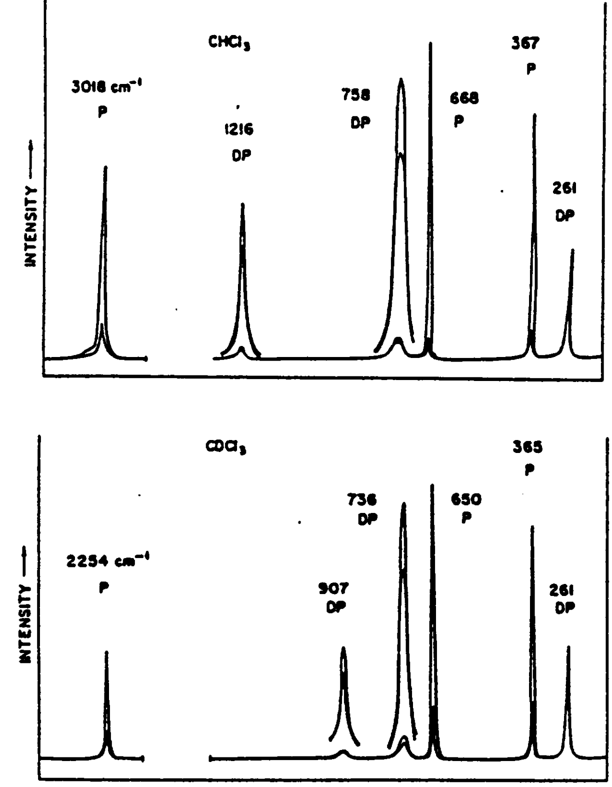

FIG. 1.35. Polarized Raman spectra of $CHCl_3$ and $CDCl_3$. The less intense spectra are run with perpendicular polarization and the more intense spectra are run with parallel polarization. The depolarization ratio is $\frac{3}{4}$ for the depolarized bands (marked DP) and is between 0 and $\frac{3}{4}$ for the polarized bands (marked P), the latter belonging to the totally symmetric species. The weaker bands (1216, 758, 907, and 736 cm^{-1}) have been rerun with higher gain. The incident radiation is from a laser source and is plane polarized.

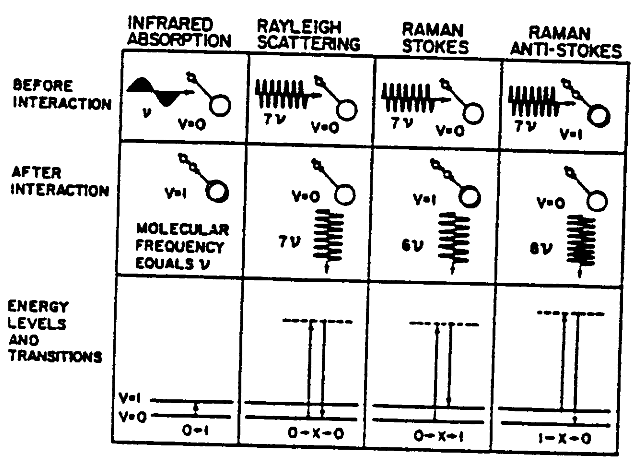

FIG. 1.30. Schematic illustration of Raman and Rayleigh scattering and infrared absorption. In infrared absorption the incident photon has the same frequency as the molecular vibration. In Rayleigh and Raman scattering, the incident photon has much higher frequency (7ν in this figure). The scattered photon is like the incident photon in Rayleigh scattering but in Raman scattering the scattered photon has a lower or higher frequency ($7\nu \pm \nu$). The photon frequency difference is the same as the molecular vibrational frequency.

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GROUP FREQUENCIES IN RAMAN SPECTRA

Amines

The IR spectra of primary amines are occasionally obscured by intramolecular hydrogen bonding or OH groups, so that the 1° amine doublet at 3300 cm^{-1} is not visible. This is never the case in the Raman spectra, so that this technique can be used for identification of substituted amines.

Alkynes

One of the most difficult lines to see in IR spectra is the C≡C stretch of interior alkynes. Terminal alkynes give a C—H stretch at 3270–3315 cm^{-1}, but nonterminal alkynes show only a weak IR peak at 2200–2260 cm^{-1}. As the interior alkynes become more and more symmetrical, this line becomes much stronger in the Raman spectrum and represents an important identification technique for these compounds. The C≡C stretch in 3-hexyne would be totally invisible in the IR as shown in Figure 10.3*a*, but is shown as a strong absorption at 2233 cm^{-1} in the Raman spectrum in Figure 10.3*b*.

Nitriles

Some C≡N stretching lines become extremely weak in the IR when the α-carbon bears chlorine or oxygen, but are quite strong in the Raman in the range of 2240–2260 cm^{-1}. This represents an important confirming technique for nitriles, along with ^{13}C nmr.

Alkenes

The C═C stretching frequencies of alkenes are always stronger in the Raman than in the IR spectrum. This is particularly clear in the spectrum of 1-octene shown in Figure 10.4*b* where the C═C stretch at 1645 cm^{-1} is most prominent. Furthermore, the depolarization ratios can help prove the substitution of the double bond, as shown in Table 10.1 below.

Table 10.1 IR and Raman Characteristics of C═C Absorptions

	IR intensity	Raman ρ
$RCH{=}CH_2$	med	0.04
$R_2C{=}CH_2$	↓	0.04
cis-RCH═CHR	↓	0.05
trans-RCH═CHR	↓	0.08
tri- and tetra-	weak	0.1

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Carbonyl Compounds

While IR remains the primary method of identifying carbonyl compounds, the depolarization ratios of esters and carboxylic acids serve to set them off from other compounds in which other relevant information may be obscured (Table 10.2).

Table 10.2 IR and Raman Characteristics of Carbonyl Compounds

	IR	Raman ρ for C═O
Ketones	methyl ketones 1350–1370	0.22–0.27 acyclic, 0.28 cyclic
Aldehydes	C—H 2695–2900	0.24–0.28
Esters	1000–1250	0.1
Carboxylic Acids	OH at 3000	0.05

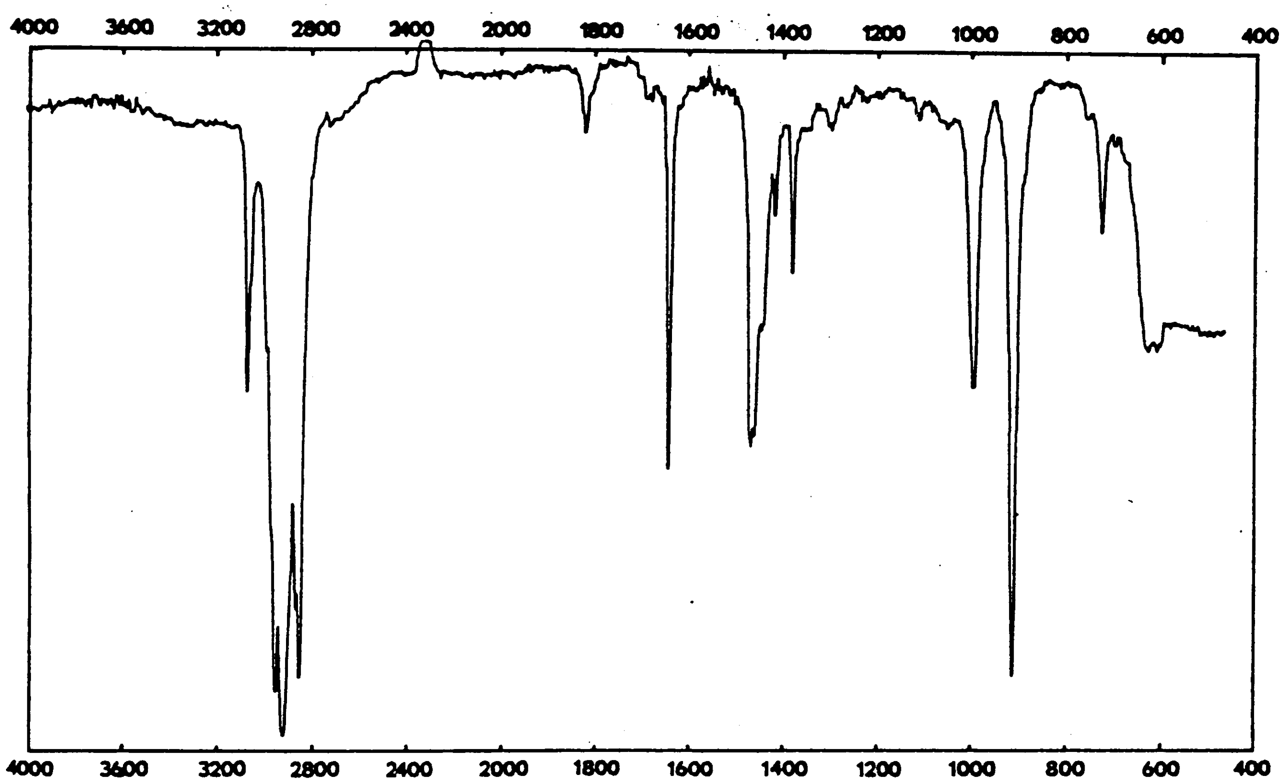
Cyclic Alkanes

Most cyclohexane compounds that are not fused to other rings show a strong ring breathing frequency in the Raman at 700–800 cm^{-1}. This is illustrated in Figure 10.5 for cyclohexane.

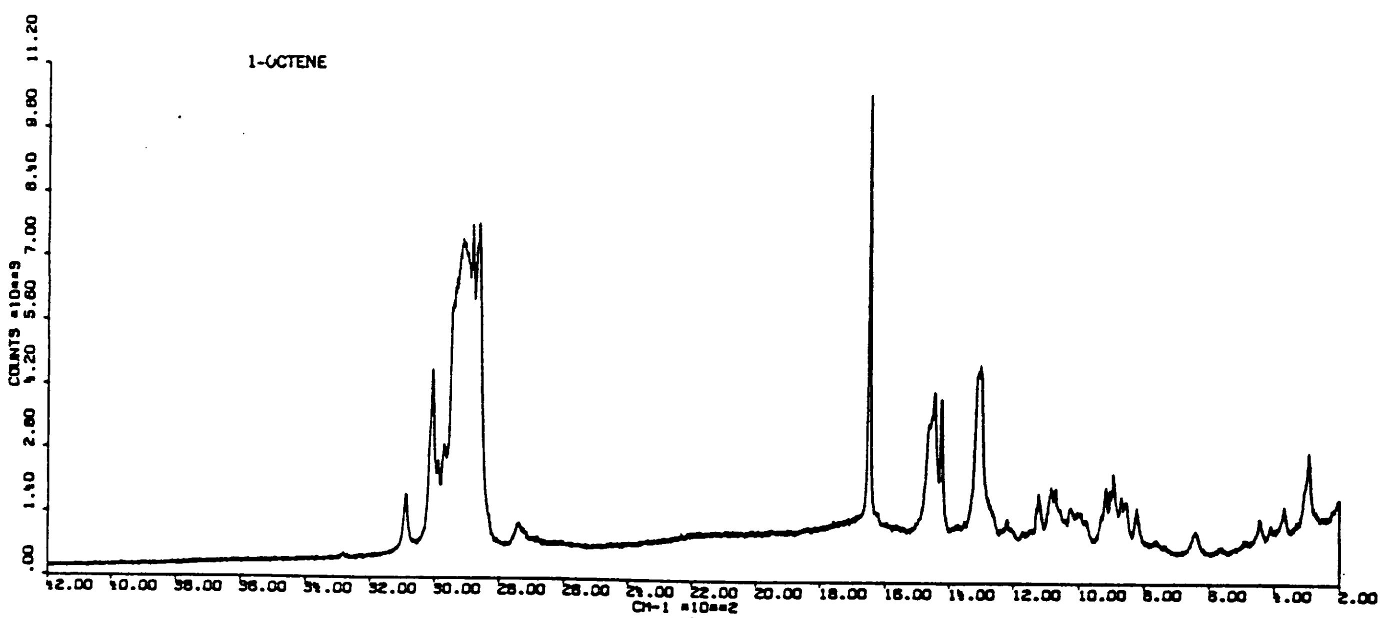
Aromatic Compounds

The following lines may be used to identify some of the common benzene substitution patterns:

	Raman line (cm^{-1})	ρ
ortho	1020–1050	0.03
	640–760	
meta	990–101	0.1
para	625–645	0.2
mono	899–1006 vs	
	1021–1035 m	
	605–625 w	



(a) IR Spectrum



(b)

Figure 10.4 (*a*) IR and (*b*) Raman spectrum of 1-octene.

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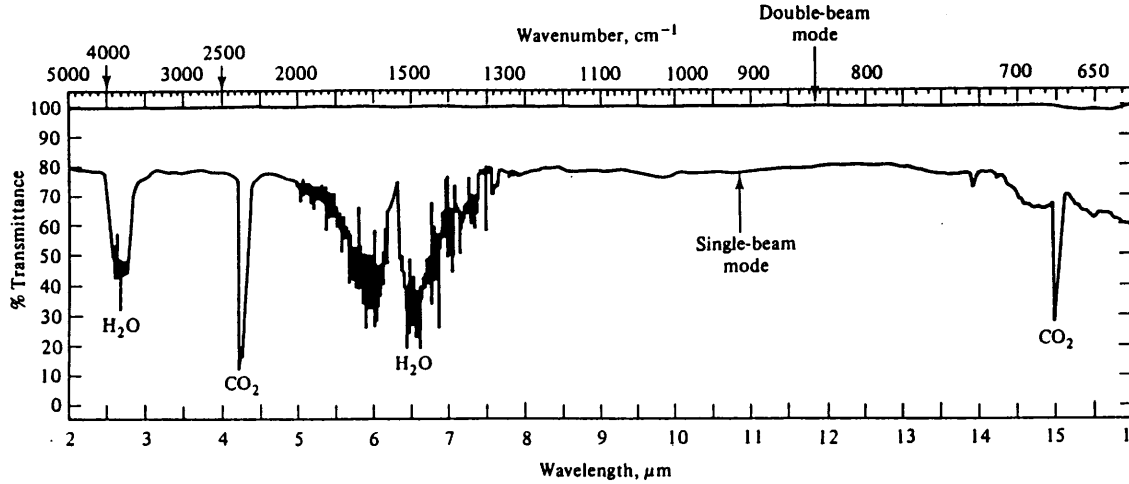


FIGURE 14-4 Single- and double-beam spectra of atmospheric water vapor and CO_2. In the lower, single-beam trace, the absorption of atmospheric gases is apparent. The top, double-beam trace shows that the reference beam compensates nearly perfectly for this absorption and allows a stable 100% T baseline to be obtained.

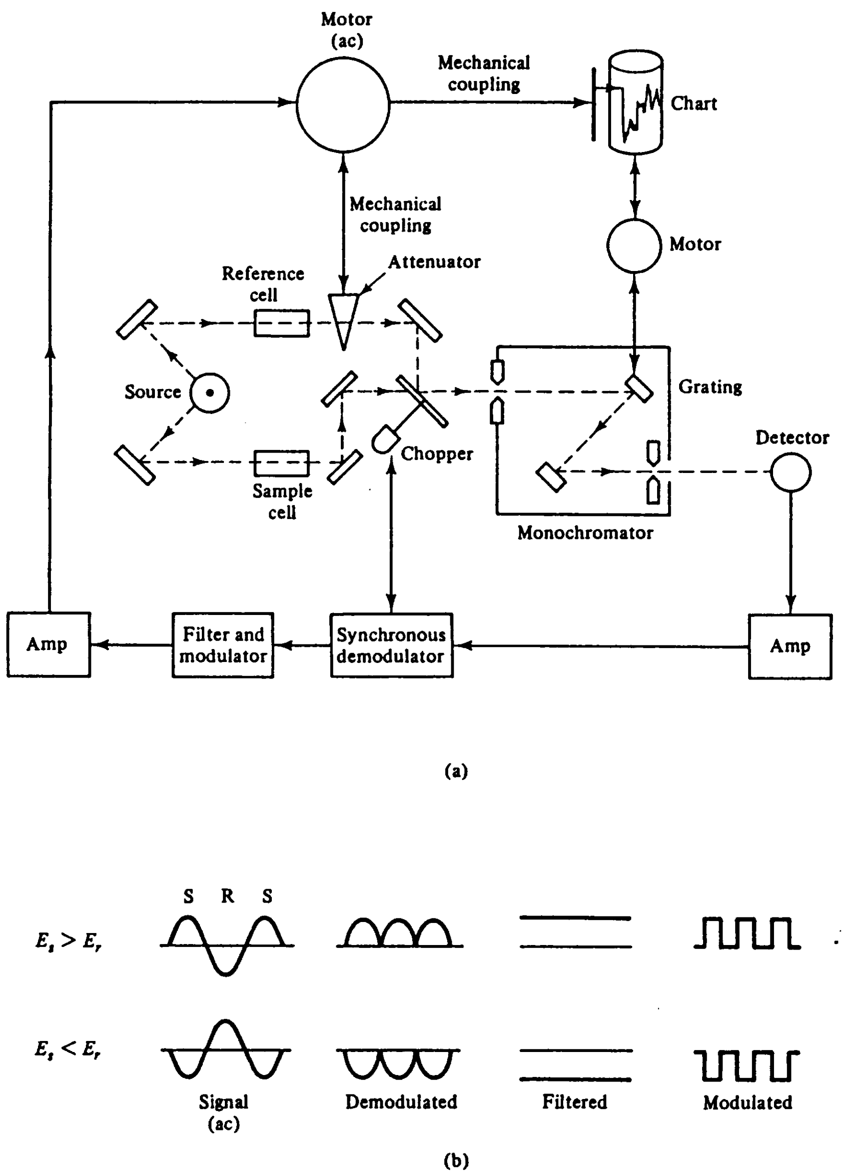


FIGURE 14-5 Optical null double-beam spectrophotometer for infrared absorption measurements. In (a), the radiation from the source is split into two beams. One beam passes through the reference cell and the other through the sample cell. The beams are recombined and chopped prior to passing alternately through the monochromator and striking the detector. Any difference in the intensity of the beams causes an ac signal from the detector, which is amplified and synchronously demodulated (b). The sign of the dc output of the synchronous demodulator (lock-in amplifier) depends on the phase of the ac demodulator input, which in turn depends on which beam is more intense. The dc output can be further amplified to drive a dc motor which is connected to a beam attenuator and the pen on the recorder. Alternatively, the dc signal can be remodulated by an electrical chopper and applied to one winding of an ac motor. The other winding is attached to the same signal that drives the electrical chopper. In either case, if the reference beam intensity is higher than the sample beam intensity, as in the lower ac signal in (b), the motor turns in the appropriate direction to move the attenuator further into the reference beam and reduce its intensity. Similarly, if the sample beam intensity is higher, as in the upper ac signal in (b), the attenuator is pulled back so as to increase the reference beam intensity.

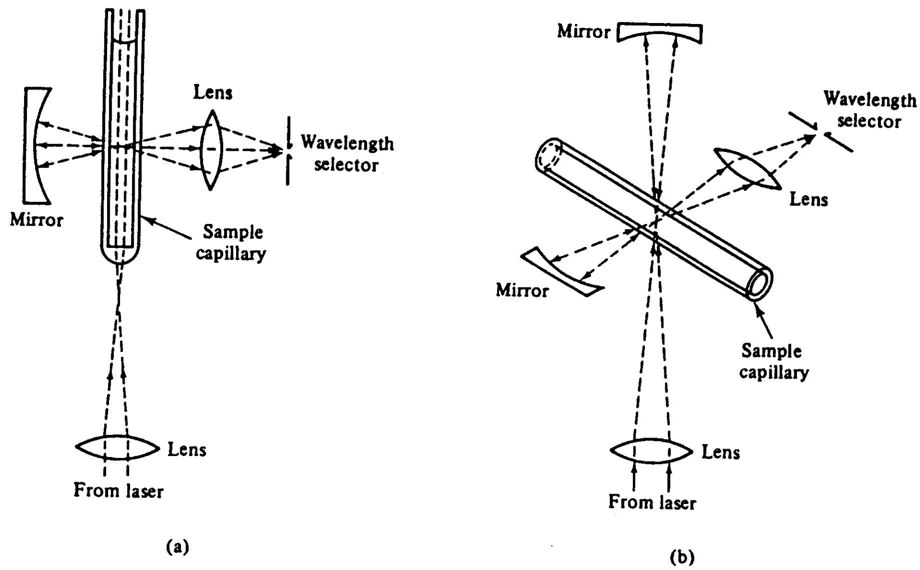
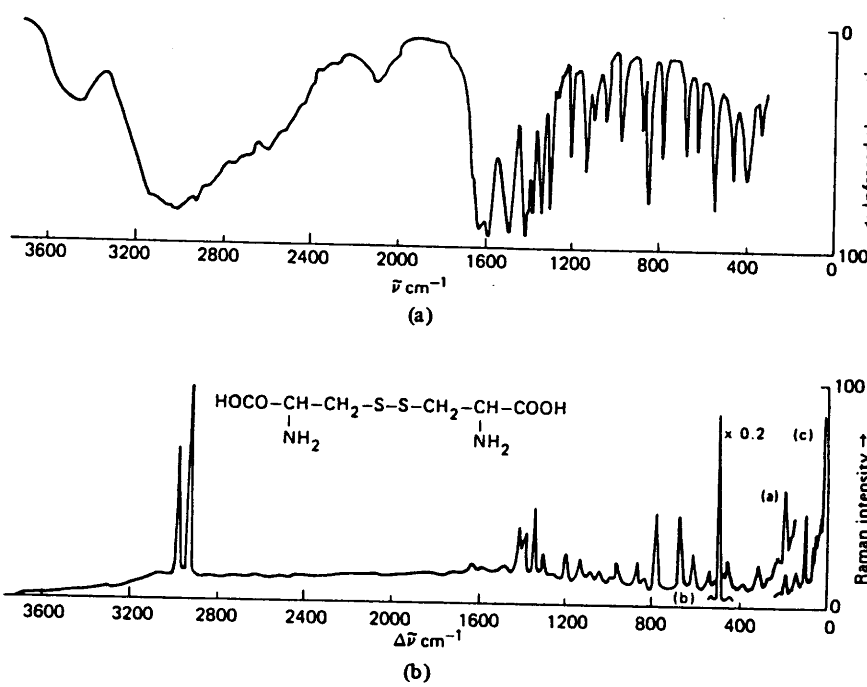


FIGURE 16-8 Cell configurations for Raman spectra of micro samples. In (a) the laser beam enters through the bottom of the capillary cell. The cell bottom serves as a lens to collimate the laser radiation. The scattered radiation is collected at 90° to the excitation beam and focused with a lens onto the wavelength selection device. Note that this arrangement provides a long pathlength for excitation and viewing along the monochromator slit width. Sample volumes can be as small as 0.04 μL. In (b) the laser beam enters the cell from the side and is reflected by a mirror to traverse the cell again. Transverse excitation simplifies alignment and allows the used of open end capillary tubes. The scattered radiation is again collected at right angles to the laser beam. With this geometry, sample volumes can be as small as 0.008 μL.



Comparison of Raman and IR Spectrometry

Although the spectra obtained by Raman scattering and IR absorption spectrometry have much in common, there are also many important differences between the two techniques. This is especially true when one considers the instrumentation and techniques for sample handling. Some of the advantages of Raman in comparison to IR spectrometry include:

1. Water is a useful solvent in Raman spectrometry, whereas it is generally a poor solvent for IR studies.
2. The optics and cell materials for Raman spectrometry are made from glass or quartz instead of the salts used in IR measurements. This greatly simplifies sample handling for Raman methods.
3. The properties of the laser sources used in Raman spectrometry make it relatively easy to probe micro-samples, surfaces, films, powders, solutions, gases, and many other sample types.
4. Transducers in Raman instruments are standard UV-visible devices (PMTs, diode arrays, etc.) instead of the thermal detectors employed in IR spectrometry. Since Raman detectors respond very rapidly, Raman spectrometry can be used to study short-lived or transient species and to follow the kinetics of rapid reactions.
5. A single Raman spectrometer can cover the entire range of vibrational frequencies, whereas even with FTIR systems, changes in detectors or beam splitters must be made to cover this range. With conventional IR spectrophotometers, two or more instruments must be used over this range.
6. Raman spectra are usually much simpler than IR spectra because overtone and combination bands are not very intense. Overlapping bands are thus much less common.
7. Totally symmetric vibrations can be observed with Raman spectrometry, whereas they are not with IR spectrometry.
8. Polarization measurements add an extra dimension to the information obtained by Raman spectrometry. This aids in band assignments and structure determinations.
9. Raman intensities are directly proportional to concentration and to the laser power.

On the other hand, IR spectrophotometry is still widely used for many applications. Among the advantages of IR over Raman spectrometry are:

1. Because of the intensity of overtone and combination bands, IR spectrophotometry is more sensitive to small structural differences. Hence it is more useful in qualitative analysis and complementary to Raman spectrometry for structural elucidation studies. Extensive libraries of infrared spectra have been compiled.
2. Infrared instruments are generally less expensive than Raman instruments. Raman measurements are susceptible to spectral artifacts from grating imperfections (e.g., ghosts) and other sources. The monochromators used in Raman spectrometers must be of higher quality than those used in IR spectrometry. Alignment is often simpler with IR spectrophotometers.
3. Because Raman spectra depend highly on laser power, cell geometry, and instrument characteristics, it is difficult to compare Raman intensities from instrument to instrument. With IR spectrophotometers, the nature of absorption measurements (e.g., ratio measurement) makes this comparison easier.
4. Detection limits for IR spectrometry are often superior to those obtained with Raman spectrometry unless resonance enhancement (see later in this section) is utilized. Neither technique is considered particularly good for trace analysis.
5. The efficiency of the Raman process is quite low. Even in favorable situations a very small fraction (e.g., 10^{-8}) of the incident photons are converted to scattered photons. As a result, broadband fluorescence emission can completely obscure the Raman signals.

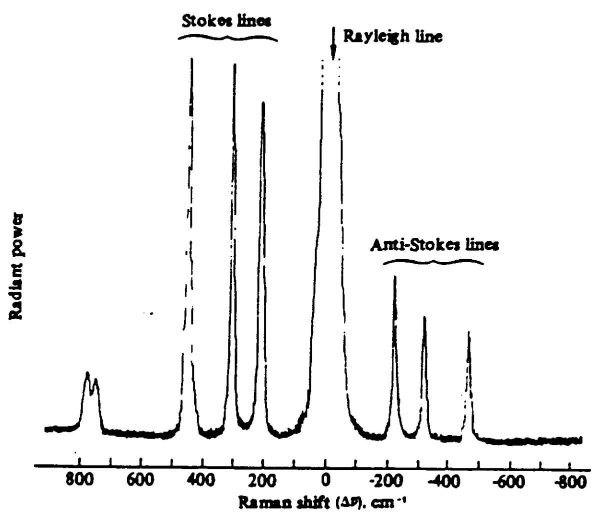
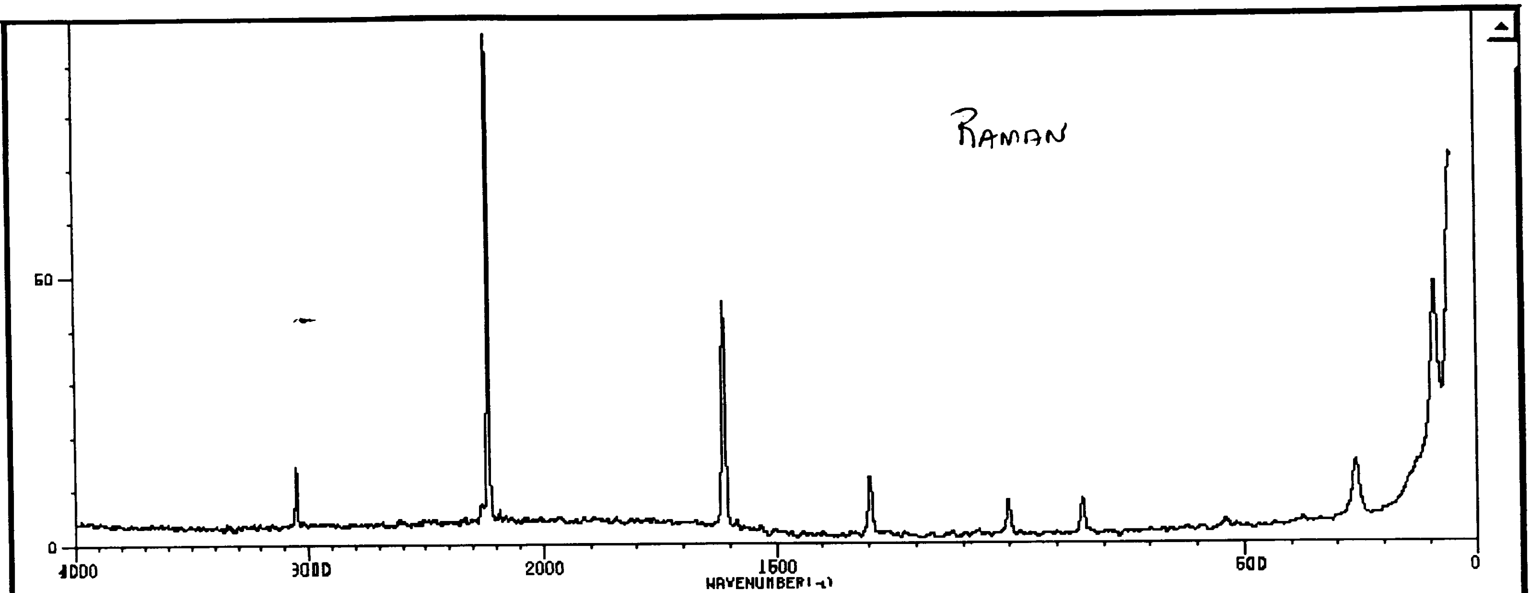


FIGURE 16-6 Raman spectrum of pure carbon tetrachloride. This spectrum was obtained with an He-Ne laser and 3 μL of sample. The Raman shift ($\Delta\bar{\nu}$) is the difference in wavenumbers between the Rayleigh line and the Raman line. [Redrawn with permission from B. J. Bulkin, *J. Chem. Educ.*, *46*, A781 (1969).]

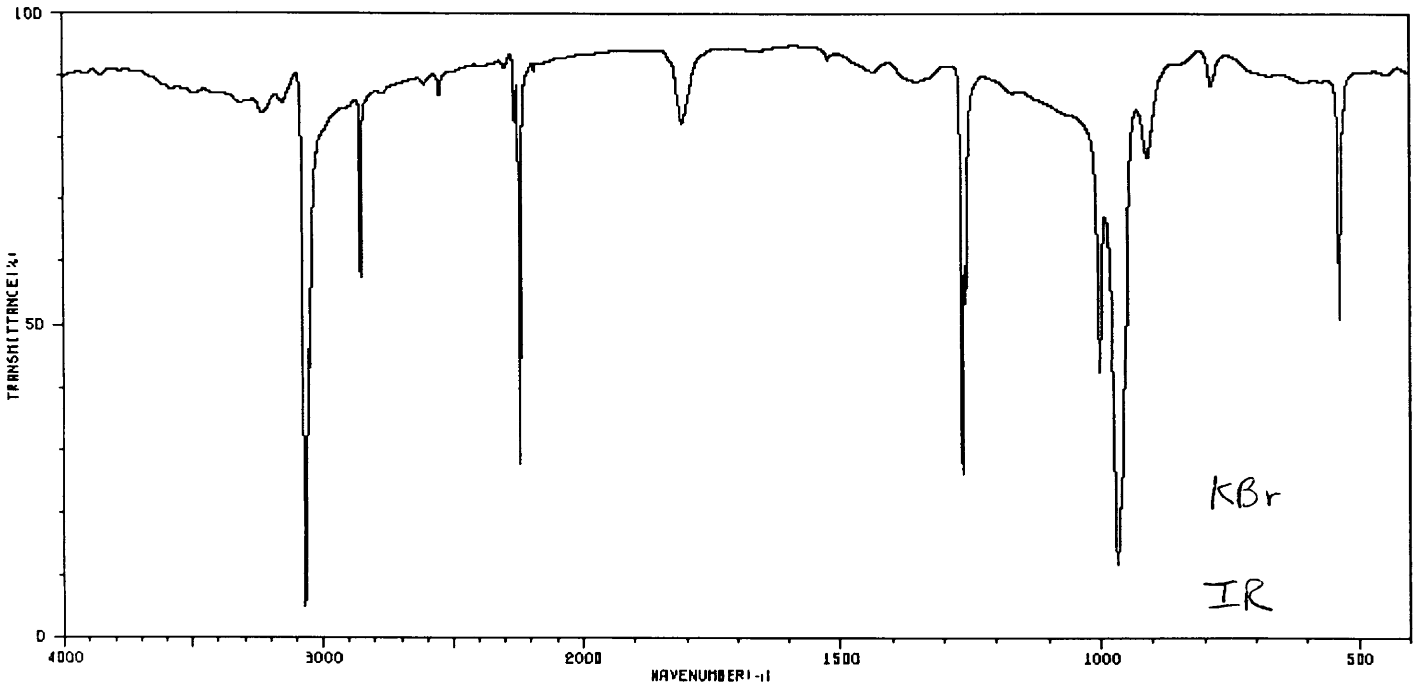


FUMARONITRILE

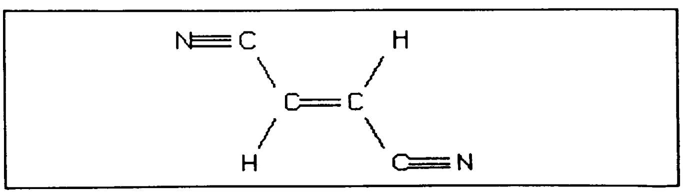
SDBSNO = 3636 $C_4H_2N_2$ RM-01-02087 : 4880A.200M.POWDER

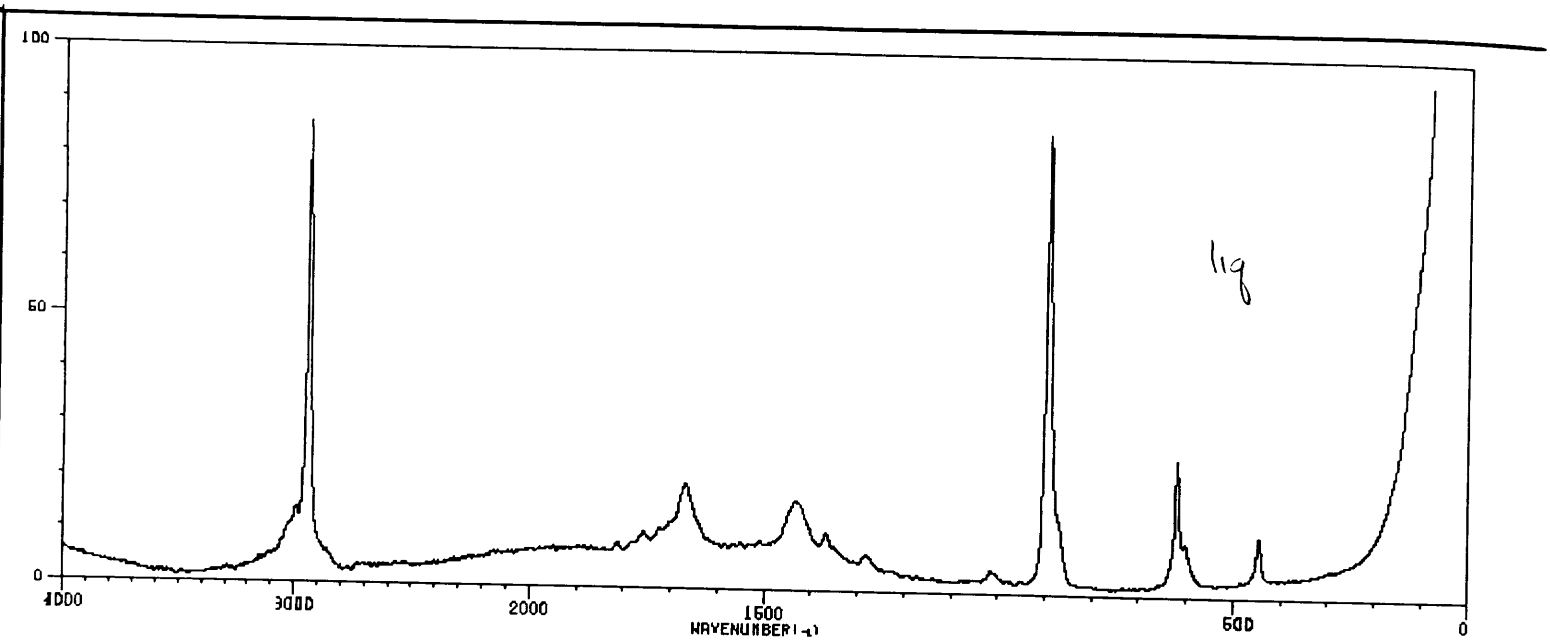
3061	14
2233	96
1613	45
1299	12
263	14
91	48

$C_4H_2N_2$



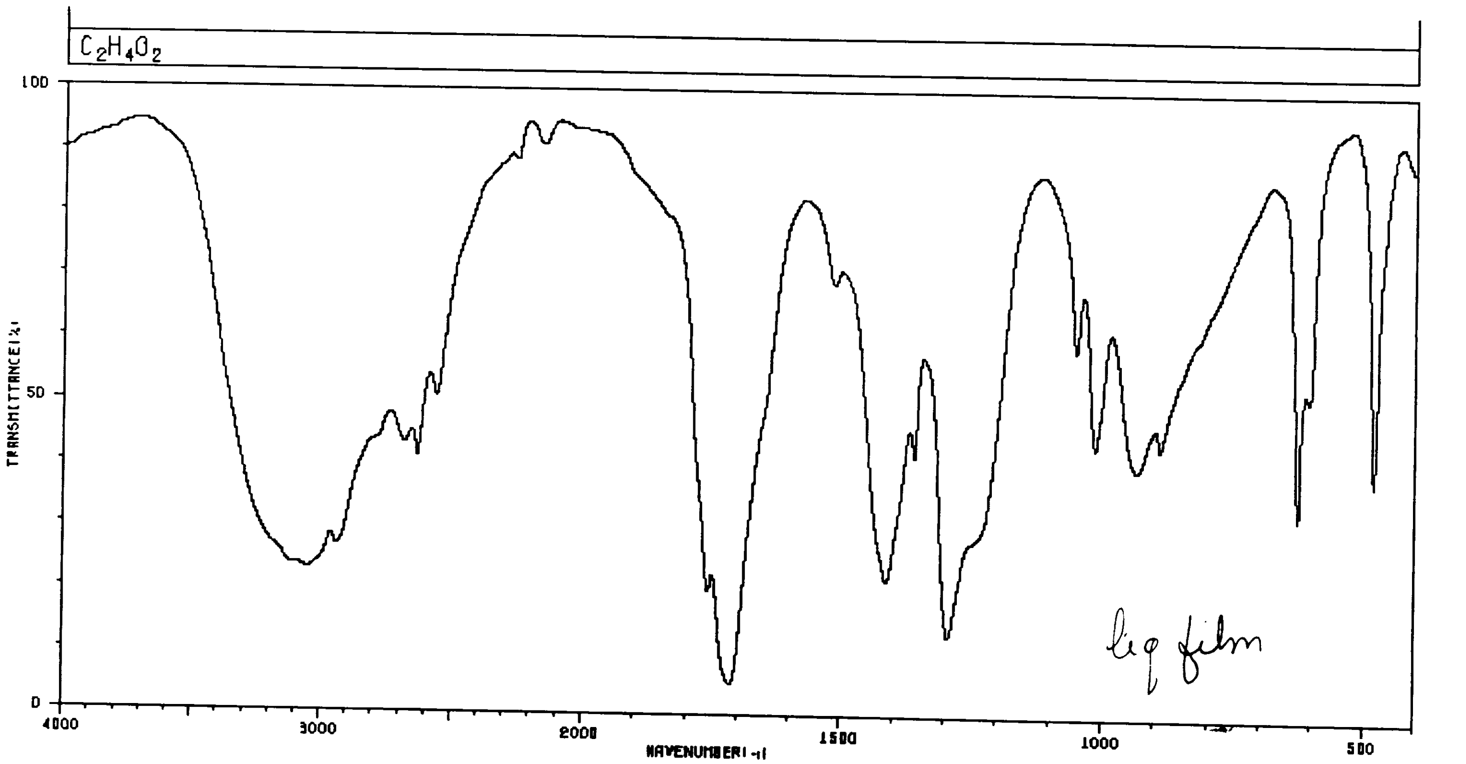
3224	81	2260	79	967	11
3150	81	2241	26	908	74
3067	4	1808	79	786	84
3048	41	1796	81	638	49
2852	55	1265	25	531	79
2805	84	1258	52		
2660	84	1001	41		



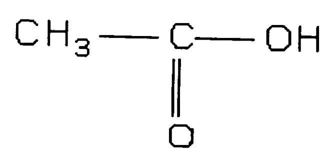


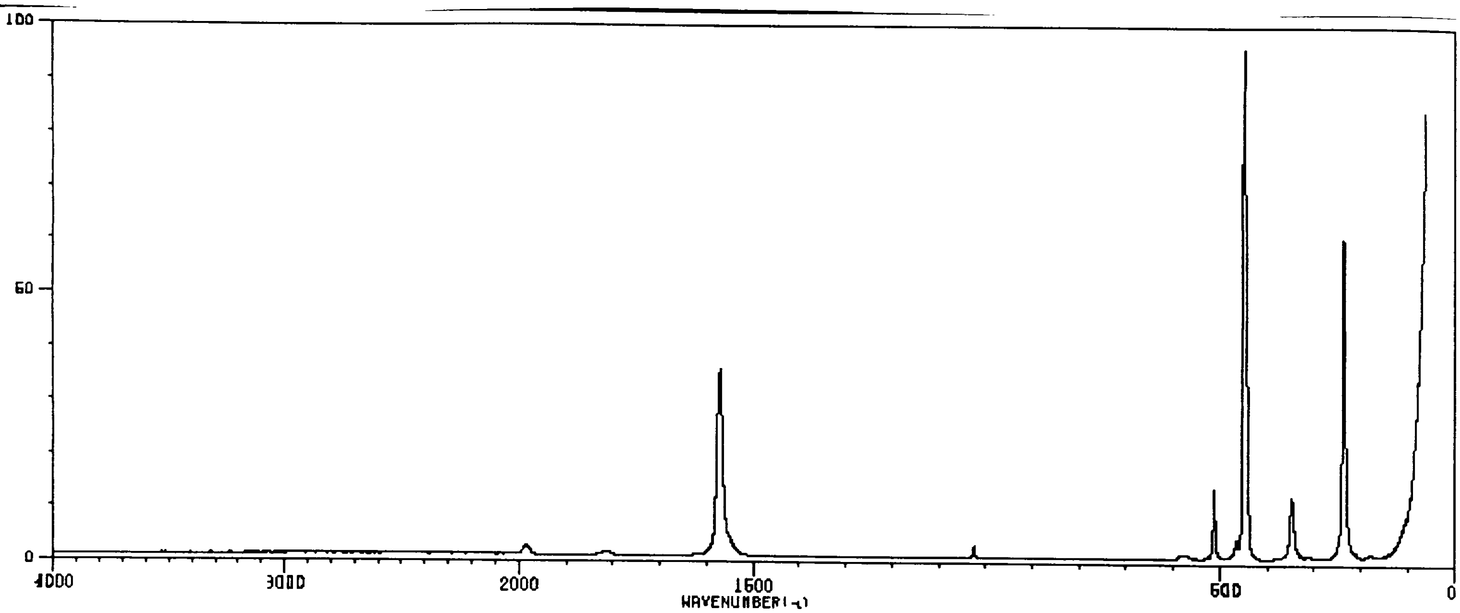
ACETIC ACID
SDBSNO = 306 $C_2H_4O_2$ RM-01-00559 : 4880A.200M.LIQUID

2944	86
896	84
623	25
448	11



2937	26	1414	20	629	31
2684	41	1360	39	607	49
2631	39	1294	12	481	36
2669	49	1063	67	473	62
1758	19	1016	41		
1714	4	935	37		
1617	66	892	41		



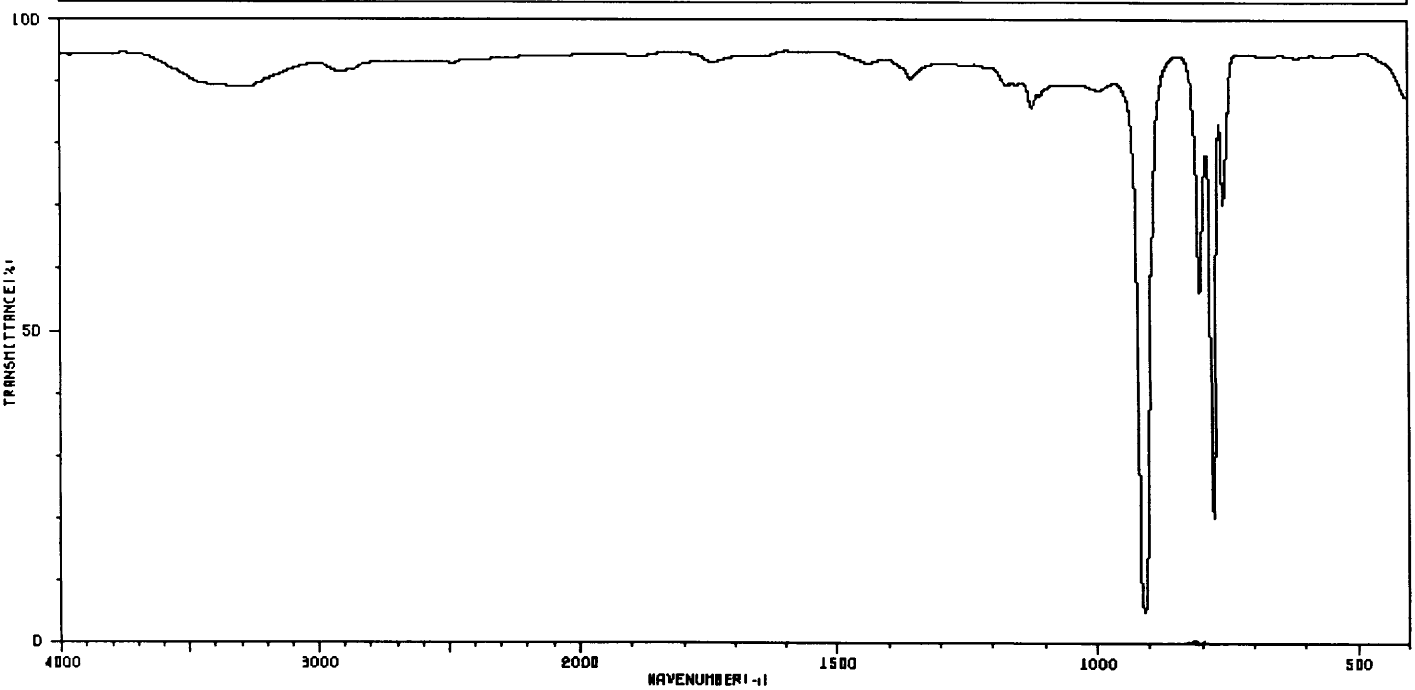


TETRACHLOROETHYLENE

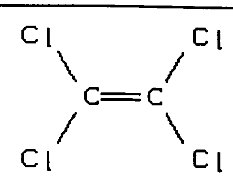
SDBSNO = 1532 C_2CL_4 RM-01-00033 : 4880A.100M.LIQUID

1573	34
613	14
450	95
349	12
237	60

C_2CL_4

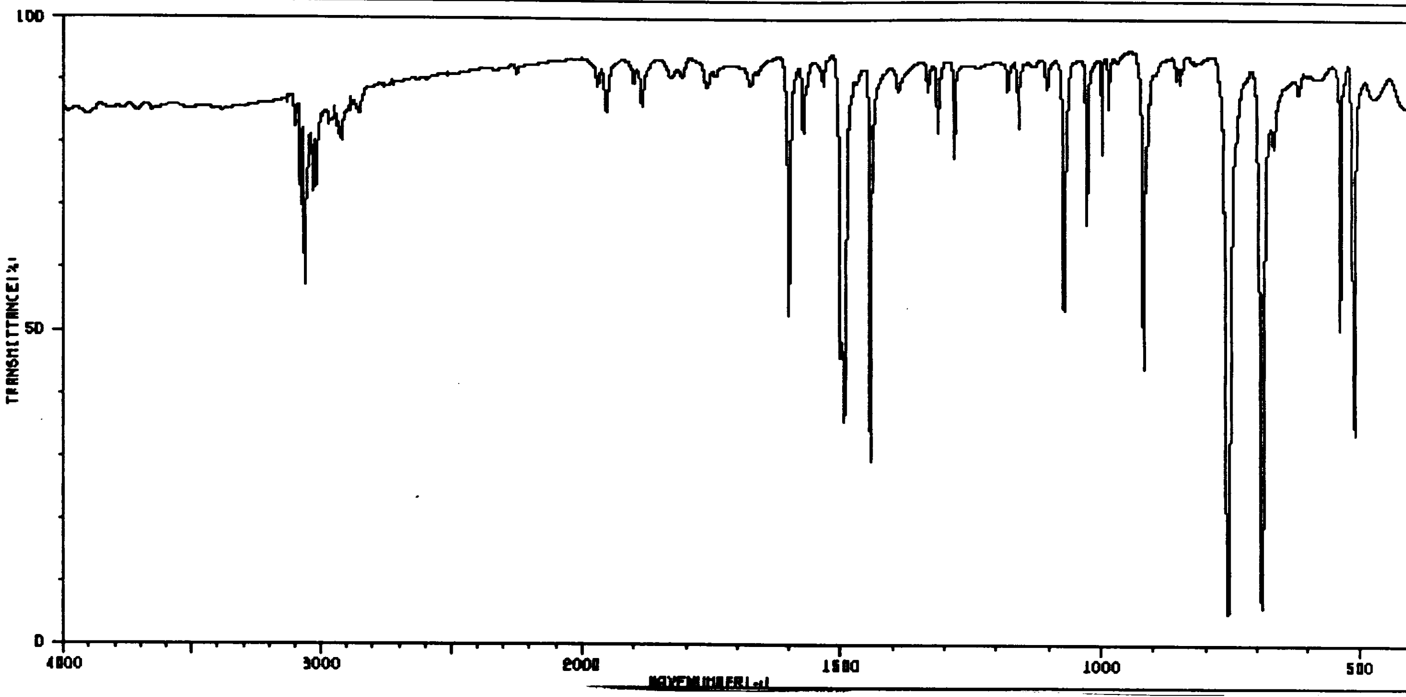


1123	81
1117	84
1107	84
910	4
802	53
778	19
767	68

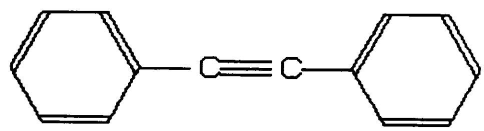


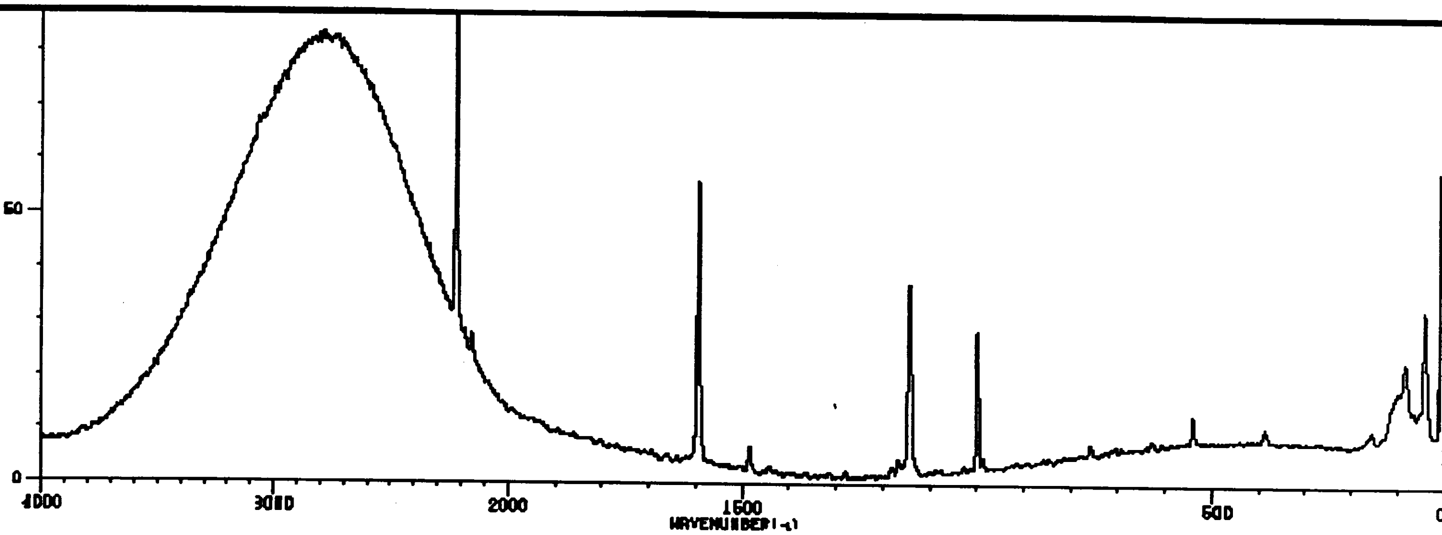
DIPHENYLACETYLENE

$C_{14}H_{10}$



3908	81	3020	70	1961	81	1434	81	986	81
3099	79	2969	79	1882	81	1313	79	918	42
3079	68	2934	79	1800	50	1281	74	757	4
3064	66	2921	77	1672	79	1167	79	691	6
3053	68	2885	81	1500	43	1071	52	667	77
3042	74	2865	81	1494	34	1026	64	536	49
3032	70	2863	81	1443	28	998	74	509	32





DIPHENYLACETYLENE

SDBSNO = 2112 $C_{14}H_{10}$ RM-01-00257 : 4880A.100M.POWDER

2922	78	84	22
2806	83	41	32
2418	53		
2225	95		
2168	27		
1596	66		
1143	37		
1000	28		
541	12		
386	10		