

Equipment for High-Pressure Infrared Measurements

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Since vibrational frequency shifts in liquids, produced by solvents and/or high liquid densities, are relatively small, precision equipment and techniques must be used. Design and operation of modified equipment, including a long path grating monochromator, a pressuring system and cells for pressures up to 5000–10 000 atm are described. A static measurement technique, involving precise positioning of the grating and read out of the transmittance on a digital voltmeter, followed by computer processing of the series of points which describe the absorption peak to determine the $\bar{\nu}_0$, are also described. Experimental data on C=C vibration on *cis*-pentene-2 are presented to illustrate results.

INDEX HEADINGS: High pressure infrared instrumentation; Pressure effects on the C=C vibrations in *cis*-pentene-2; Frequency shifts.

INTRODUCTION

Infrared shifts, between free vibration in the low pressure gas and hindered vibration in the liquid and the compressed liquid, can be used to determine the field potential in which a molecule moves in the liquid state. For these purposes shifts must be determined to four significant figures; since the magnitude of the shifts involved are 0–20 cm^{-1} this means that 0.001–0.01 cm^{-1} must be discernible. Equipment components and techniques of an experimental system to study such shifts must be optimized in order to obtain the required precision; for example, automatic scan methods cannot be used, a fact which is indicated in the literature^{1–3} and confirmed by our experience. Reproducibility to the desired precision of position and shift is almost impossible by automatic scan methods; instead static measurements followed by curve fitting of the absorption peaks were required.

I. EXPERIMENTAL

A. Spectrophotometer

The spectrophotometer used is a modified Beckman IR-5A. The source, detector circuit, amplifier, filter, servomotor, servoamplifier, electromechanical assembly, and part of the optical system were incorporated in the modified double-beam spectrophotometer. The prism monochromator of the Beckman IR-5A was replaced by a longer-path, higher-resolution, grating monochromator. The major new and modified parts of the equipment described herein are (1) the monochromator, (2) energy source, (3) pressuring system, and (4) high-pressure cells.

A diagram of the spectrophotometer is shown in Fig. 1. The grating monochromator was designed by

a trial and error graphical procedure, assuming a point source at the entrance slit. Both optical and mechanical feasibility were considered in the design. The light beam is focused at the exit slit, so that the energy loss is minimal, which requires that all mirrors and the gratings must be at the right levels and angles, and the forward and backward path lengths must be equal. In order to recover the maximum energy in the monochromator, the vertical optical configurations were also considered, requiring all optical components to be large enough to cover the light band.

The focal length of the monochromator is 50 cm, which is a compromise between the resolution power and the intensity of energy at the detector. The longer the focal length the higher the resolution, but less energy arrives at the detector. The forward optical path (entrance slit to grating center) is 93.40 cm, and the backward optical path (grating center to exit slit) is 93.56 cm. The collimator holder was designed so that its position can be adjusted to a $\frac{1}{4}$ in.

The 100-cm radius of curvature collimator has its axis 7.4° off the entrance slit axis and is a compromise between the space available to mount and rotate the grating and the convergency of the light band.

The collimator accepts light from the entrance slit and reflects it to the plane diffraction grating which disperses it into component wavelengths. At any given angular position of the grating, there is a beam of a narrow, wavelength light going back to the collimator and being reflected to the exit slit. The beam passes the slit and optical filter, which eliminates the second and higher order diffraction, and finally reaches the detector.

Two standard plane reflectance gratings with ruled areas of 64×64 mm, manufactured by Bausch & Lomb, Inc.⁴ were used: grating A, 300 grooves/mm, 2–5 μ range, blazed at 3.5 μ (31° 40'); grating B, 100 grooves/mm, 5–8 μ range, blazed at 7.5 μ (22° 2'). Since only first order diffraction was involved and the incident and diffracted rays fall on the same side of the

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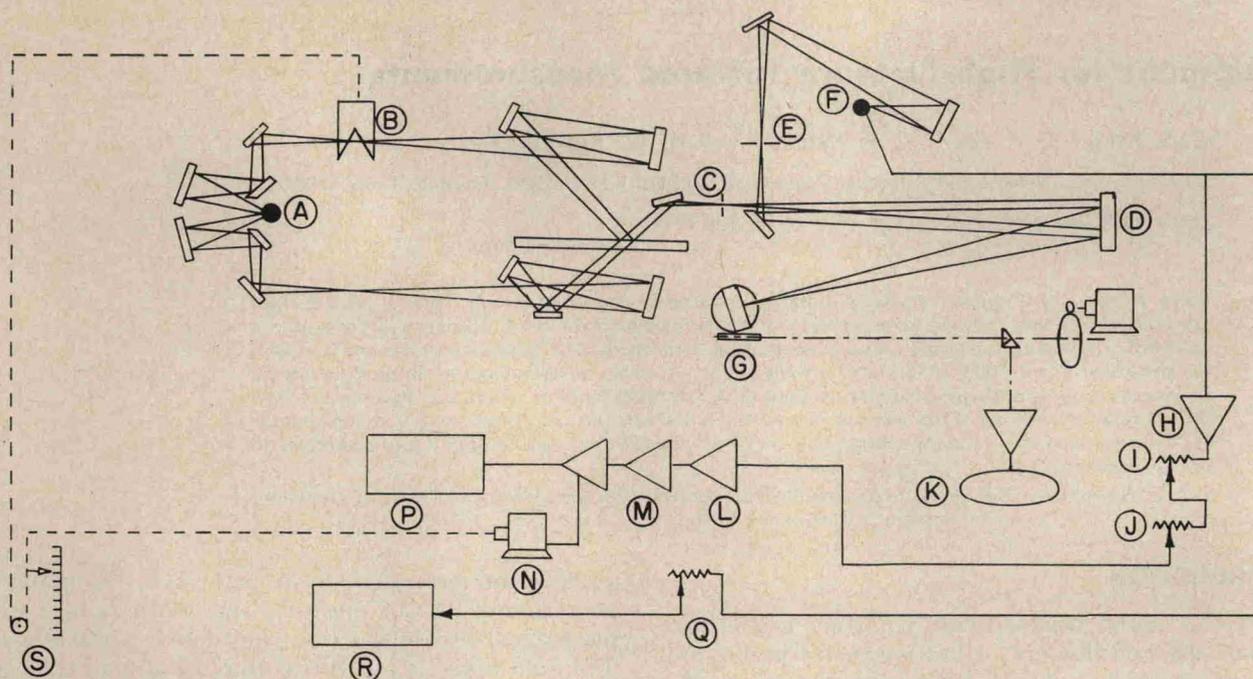


FIG. 1. Spectrophotometer diagram: (A) source; (B) comb; (C) entrance slit; (D) collimator; (E) exit slit; (F) detector; (G) grating; (H) preamplifier; (I) auxiliary gain; (J) gain; (K) calibrated dial; (L) voltage amplifier; (M) servoamplifier; (N) servomotor; (P) power supply; (Q) signal trimmer; (R) digital voltmeter; (S) auxiliary reading.

normal, the grating equation becomes

$$n\lambda = a(\sin\alpha + \sin\beta), \quad (1)$$

where

- n = order of diffraction, integer
- λ = wavelength, microns
- a = grating spacing, microns
- α = angle of incidence

and

- β = angle of diffraction.

From direct measurement on the optical diagram, the difference between the incident and diffracted angles, $(\alpha - \beta)$, is approximately 1.15° .

From the equation it is obvious that for any set of α and β , there is not a unique wavelength going to the detector, but all light with wavelengths λ/n where $n=1, 2, 3, \dots$. In order to obtain sharp and clear peaks in the spectra, n must be limited to one fixed number.

A long wavelength pass optical filter is used behind the exit-slit to eliminate all second and higher order light; only first order diffracted light $n=1$, passes the filter and reaches the detector. The filter also eliminates short-wavelength stray light.

Three long wavelength pass filters, supplied by Optical Coating Laboratory, Inc., are used; their critical wavelengths are 2.220, 3.970, and 5.080 μ , and they have approximately 80% average transmittance in wavelength ranges of 2.35–5.00 μ , 4.04–7.85 μ , and 5.36–10.70 μ . The filters were designed for use at 20°C and 0° angle of incidence using collimated energy; deviations therefrom alter the spectral shape

of the filter and shift it to longer or shorter wavelengths⁵; however, these variations have negligible effect in this application.

The grating can be rotated either by the synchronous motor or manually. When the grating shaft is engaged with the motor through the clutch, a 0–100-mV dc signal is sent to the recorder and automatic recording scanning is obtained; this process gives a continuous spectrogram.

The synchronous motor can rotate in both directions at 1 rpm, depending on the switch setting. It turns the worm at the constant speed $1/480$ rpm or $\frac{3}{4}$ deg/min, and gives the scan speed approximately $63.2 \text{ cm}^{-1}/\text{min}$.

When the shaft is engaged with the manual drive, the grating can be rotated by hand through two planetary drive mechanisms in series, each having a drive ratio of 5:1. One scale division on the calibrated vernier dial corresponds to 0.021841 cm^{-1} , and one revolution of the dial equals 4.3681 cm^{-1} . At each fixed angular position of the grating, the signal is read out from a 0–100-mV digital voltmeter (model DVM-4000, Trymetrics Corporation), which has a minimum sample time of 3 sec and an output of four digits.

The entrance and exit slits are used to define a narrow light image and increase the resolving power of the monochromator. Each slit consists of two pieces of metal having sharply machined edges facing each other. The aperture of sharp edges is one of the key factors which determines the resolution and intensity of energy falling on the detector. The slits are operated bilaterally to keep the apertures the same. An unequal slitwidth may cause trapezoidal spectral lines.⁶

The minimum wavelength or wavenumber interval which the monochromator can resolve is expressed by the spectral slit width, which can be calculated from the following equation³

$$\Delta\bar{\nu}_s = \bar{\nu}^2 \frac{d \cos \alpha s}{2n f} + F(s) \frac{\bar{\nu}}{Mn}, \quad (2)$$

where

$\bar{\nu}$ = wavenumber, cm^{-1}

$\Delta\bar{\nu}_s$ = spectral slit width, cm^{-1}

d = grating constant, distance between successive lines, cm

s = slit aperture, cm

f = focal length, cm

M = total number of lines on the grating

and

$F(s)$ = slit width function.

The exact nature of $F(s)$ is in doubt; as a first approximation it is assumed to be linearly depending on the slit width, having values of 0.9–0.5 for narrow to wide slit widths, respectively. The first term in the equation is called the slit-limiting term, and the second the diffraction-limiting term; the slit term is much larger than the diffraction term, from two to 20 times greater, depending on the wavenumber.

The energy which passes through the exit slit and falls on the detector is proportional to the slit height and the square of the slit width. Therefore, a wider slit width gives a stronger signal to operate the mechanical servo assembly, but it also causes a poorer resolution.

Since the focal length of the monochromator was extended from 35 to 40 cm, a stronger light source was required. The radiant power falling on the detector³ is given by the equation

$$P_\nu = \frac{B_\nu h s^2 A T_\nu \nu^2}{16\pi f^3 c (d\theta/d\lambda)}, \quad (3)$$

where

P_ν = the radiant power falling on the detector,

B_ν = the brightness

h, s = slit height and width, respectively

A = area of collimator optical surface

f = the focal length

c = the velocity of light

$(d\theta/d\lambda)$ = the angular dispersion of the grating

ν = frequency, cps

T_ν = the efficiency of the various monochromator optical parts.

According to this equation, the radiant power on the detector is reduced to 34.3% of the original value. In order to make up this loss, the voltage across the source element was increased, with a corresponding reduction in life expectancy.

A PEN-RAY argon-mercury quartz lamp, manufactured by Ultra-Violet Products, Inc., San Gabriel,

Calif., with a special transformer, was used as the light source for the optical alignment of the monochromator. The lamp, 6.5-mm diam \times 5.08-cm long emitting tube, provides seven discrete spectral lines at 2537 Å, 3125 Å, 3650 Å, 4358 Å, 5461 Å, and 5770 Å. When the lamp replaces the light source of the spectrophotometer, the image of the lamp can be observed in the center part of the grating, and after dispersion a spectrum of different colors appears. The green light, 5461 Å, is used to align all optical components after the grating. When all components are in the correct positions and angles, the green beam is focused on the crystal surface of the detector.

B. The Pressuring System

Figure 2 is a schematic of the pressure producing apparatus and consists of two parts. The low pressure part is mounted on a relay rack panel and consists of a pump, oil reservoir, a pressure gauge and the appropriate valves.

The second part of the apparatus, a pressure intensifier shown in Fig. 3, multiplies the low pressure by a factor of approximately 16. The design is similar to one appearing in the literature by Fishman and Drickamer.⁷ The main body of the intensifier is constructed of AISI 4340 steel hardened to 50 Rockwell C. The piston arrangement is constructed of Sagamore tool steel hardened to 55 Rockwell C. Both the high and low pressure ends of the piston are sealed by the Bridgman unsupported-area principle,⁸ and the seal rings are constructed of Teflon. The low pressure is connected to the ir cell by Harwood $\frac{1}{8}$ -in. tubing and

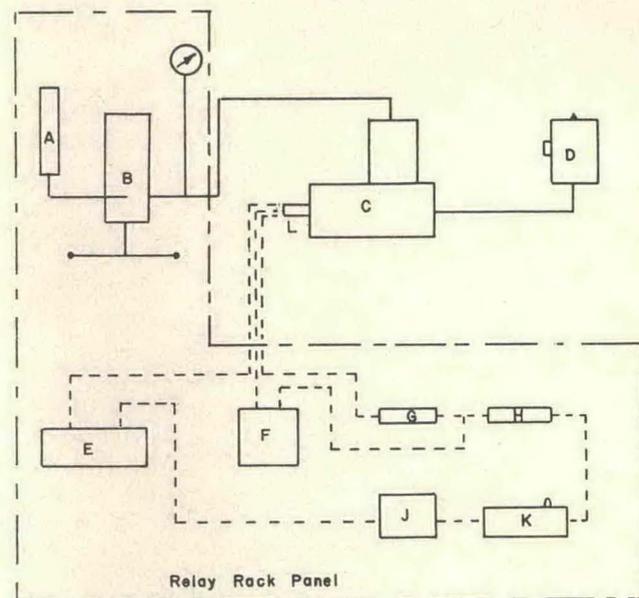


FIG. 2. Pressuring and measurement system. (A) Oil reservoir; (B) Aminco 0–15000 psi pump; (C) 16–1 pressure intensifier; (D) I–R cell; (E) Kepeo model ABC power supply; (F) L & N model 9834–1 null detector; (G) 2100 Ω resistor; (H) 2000 Ω resistor; (J) L & N model 4776 resistance box; (K) L & N model 4258 slidewire; (L) strain gauge pressure transducer.

fittings. A pressure transducer⁹ is mounted in the intensifier; between the transducer and the intensifier is a metal-to-metal conical seal. A short plug with both ends machined to 59° is fitted into 60° receptacles between the two pieces. The intensifier has been pressure tested to approximately 10 000 atm.

C. The 0–1500 Atm Cell

Figure 4 shows the 0–1500-atm variable path ir cell, which was constructed of type 303 stainless steel. Windows for the cell are either Irtran 1 or 2 obtained from Eastman Kodak Company. Three plugs were made for the cell; by choosing the proper two, the path length can be approximately 0, $\frac{1}{4}$, or $\frac{1}{2}$ in. Fine adjustment of the path length is made by varying the length of the retaining rings. The two plugs are held in place with six stainless steel cap screws each, and the pressure seal is obtained with Viton O-rings. This cell is equipped with Harwood $\frac{1}{8}$ -in. tubing fittings. Cells of the two plug type, capable of withstanding up to 12 000 atm, have been built by other investigators.⁷

D. The 1000–10 000 Atm Cell

A high-pressure cell was designed to operate under various pressures up to 10 000 atm, and consists of four major parts: body, plug, seal rings, and windows.

The cell body shown in Fig. 5 is a 4-in. cubical block, made of SAE 4140 annealed steel and heat treated to the hardness 48/52 Rockwell C. The beam of light path through the cell is 0.203 in. and the cell holds approximately 0.0205 cm³ of sample. The surface which supports and seals the window was ground and lapped to approximately 4–6 μ flat.

Because of the irregular configurations of the cell body, an exact stress analysis is quite complicated.

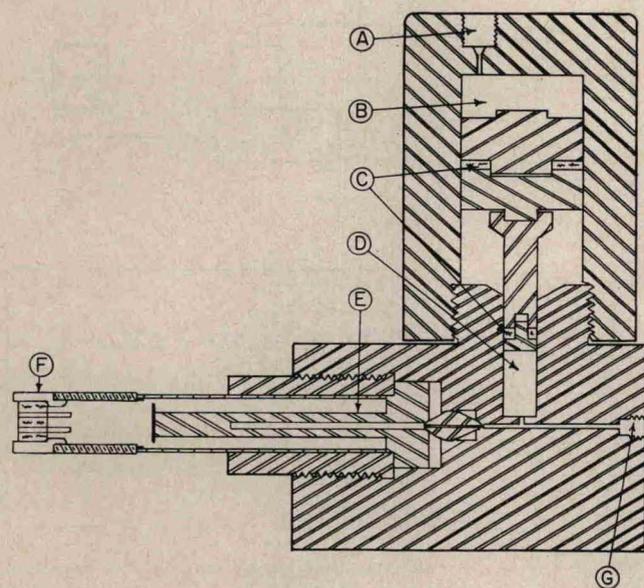


FIG. 3. Pressure intensifier. (A) Aminco $\frac{1}{4}$ -in. fitting; (B) low pressure chamber; (C) Teflon packing ring; (D) high pressure chamber; (E) pressure transducer; (F) electrical connector; (G) Harwood series 2M fitting.

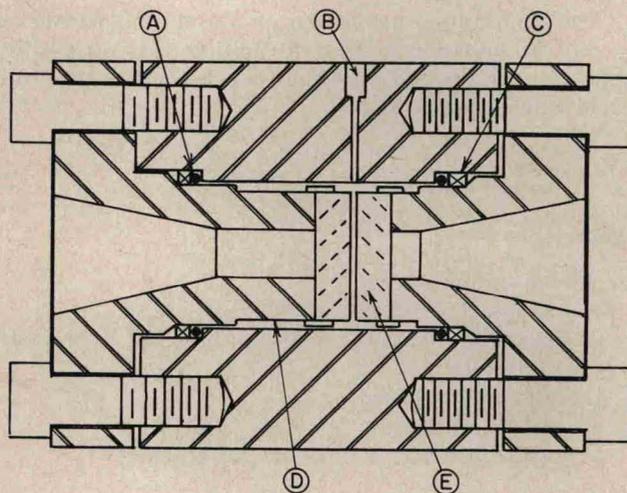


FIG. 4. 0–1500 atm cell. (A) Viton O-rings; (B) Harwood Series 2M fitting; (C) adjustable retaining rings; (D) variable plug dimension; (E) Irtran window.

However, an approximate calculation was made, and indicated that the maximum shear stress would be approximately 37 000 psi and the maximum compressive stress approximately 155 000 psi, compared to a maximum allowable shear and compressive stress for SAE 4140 annealed steel after heat treatment of 140 000 psi and 200 000 psi, respectively.

The plug, made from graph-air tool steel which has the least distortion during heat treatment, was heat treated to 58–62 Rockwell C hardness. The plug has a 1.456-in. major diam and 16 threads/in. (American National), and is 2.476 in. long. A 45° slope in the shoulder of the plug provides a free space for the deformation of the steel ring under high pressures. The end which supports the window was ground and lapped to 4–6 μ flat.

A two-stage technique is used to seal the plug based on Bridgman's⁸ pipe connection, and includes two different steel rings and one O-ring.

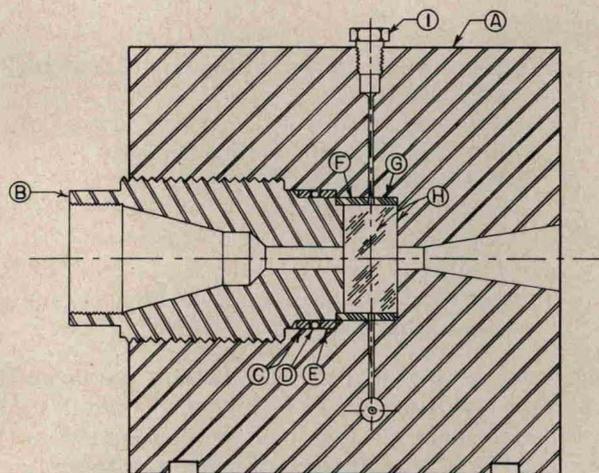


FIG. 5. High-pressure cell. (A) cell body; (B) plug; (C) steel ring; (D) O-ring; (E) steel ring; (F) Teflon ring; (G) Teflon ring; (H) Irtran windows; (I) seal plug.

Table I. High-pressure ir optical materials.

Material	Spectral range, μ	Refractive index ^a	Modulus of rupture, ^a psi	Young's modulus ^a psi	Compressive strength, psi	Hardness Knoop No.	Solubility g/100 g H ₂ O
NaCl	0.2-15	1.52 at 4 μ 1.4 at 10 μ	...	5.8 \times 10 ⁶	...	15.2-18.2	35.7(0°C)
Lithium fluoride, LiF	0.11-6	1.35 at 4 μ 1.1 at 10 μ	...	9.40-11 \times 10 ⁶	...	102-113	0.27(18°C)
Irtran 1, MgF ₂	1-8	1.35 at 4 μ	21 800	16.6 \times 10 ⁶	157 600	576	0.0076(18°C)
Calcium fluoride CaF ₂	0.13-9	1.41 at 4 μ	...	11-15 \times 10 ⁶	...	158	0.0016(18°C)
Irtran 3, CaF ₂	1-10	1.41 at 4 μ 1.34 at 8.3 μ	5 300	14.3 \times 10 ⁶	...	200	Insoluble
Irtran 2, ZnS	2-14	2.25 at 4 μ 2.20 at 10 μ	14 100	14 \times 10 ⁶	121 200	354	0.00069(18°C)
Irtran 4, ZnSe	0.5-20	2.5 at 4 μ 2.4 at 10 μ	6 100	10.3 \times 10 ⁶	...	150	Insoluble
Magnesium oxide, MgO	\leq 6.8	1.7 at 2.2 μ 1.66 at 4.3 μ	...	36.1 \times 10 ⁶	...	690-692	0.000012
Irtran 5, MgO	1-8	1.67 at 4 μ 1.60 at 6 μ	19 200	48.2 \times 10 ⁶	...	640	0.00062
Sapphire, Al ₂ O ₃	\leq 5.5	1.73 at 2.2 μ 1.68 at 4.3 μ	...	50.56 \times 10 ⁶	..	1370 1525-2000	9.8 \times 10 ⁻⁵
Ceramic barium titanate, BaTiO ₃	\leq 6.9	2.4 at 2.2, 4.3 μ	..	16.50 \times 10 ⁶
Calcite, CaCO ₃	0.2-5.5	\cong 1.7 at 1 μ	...	10.50 \times 10 ⁶ 12.80 \times 10 ⁶	0.0014(25°C)
Germanium	1.8-2.3	\cong 4.0 at 2-10 μ	...	14.9 \times 10 ⁶	Insoluble
Silicon	1-9	3.43 at 3 μ 3.42 at 5-10 μ	...	19.0 \times 10 ⁶	60 000	1150	Insoluble
Fused silica SiO ₂ (corning 7905, GE type 101-100, Infrasil)	0.3-3.5	1.43 at 2.2 μ	...	9.6-10.6, 11.1, 14.1 \times 10 ⁶	...	461, 470, 741	Insoluble
NBS F158 SiO ₂	4.5	1.80 at 2.2 μ	...	15.4 \times 10 ⁶	...	461	Insoluble
Bausch & Lomb ^b RIR-2	4.5	1.75 at 2.2 μ	...	10.2 \times 10 ⁶	...	800	...
RIR-10, 11, 12	5.0	1.62 at 2.2 μ	...	15.2 \times 10 ⁶	...	900	Insoluble
RIR-20	5.5	1.82 at 2.2 μ	...	12-14 \times 10 ⁶	...	760	...

^a 25°C.

^b Calcium aluminate (CaO-Al₂O₃) and similar materials.

Since the material of the O-ring may be soluble in the sample, a test is required; for example, silicon, butadiene, and neoprene O-rings expand and weaken in *cis*-pentene-2. A Viton O-ring, 1 $\frac{1}{8}$ in. i.d. and 1 $\frac{1}{4}$ in. o.d. (No. 2-024), is used between two steel rings, and is expected to seal in the low pressure region (up to

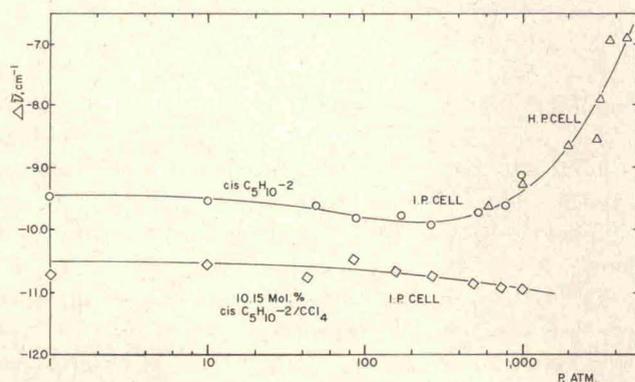


FIG. 6. Shifts of C=C vibration.

about 3000 atm). The bottom steel ring seals in the high pressure region.

The bottom ring was made of SAE 4140, heat treated to 38-42 Rockwell C, and is 1.124 \pm $\frac{0.000}{0.001}$ in. o.d. Its thickness varies from 0.197 in. to 0.222 in., depending on the desired optical path length of the cell. The free space in the shoulder of the plug permits deformation of the bottom ring, which occurs along the edge of the ring and seals the pressure when the O-ring fails to hold.

The top steel ring is made of graph-air tool steel, heat treated to about 45 Rockwell C and its o.d. and i.d. are the same as the bottom ring; the thickness is 0.125 in.

E. Cell Windows

The windows are two pieces of circular optically flat material of 1.000 \pm 0.005-in. diam and 0.250 \pm 0.004-in. thickness. The maximum operating pressure of the cell is limited by the strength of the window material and design of the cell. A summary of infrared optical

materials, whose Young's moduli are $10 \times 10^6 \psi$ or higher, is given in Table I.¹⁰⁻¹⁴ Sodium chloride is included for comparison. An equation to calculate the minimum window thickness, suggested by the Eastman Kodak Company,¹⁰ is given by

$$t = (1.1Pr^2/S_a)^{1/2}, \quad (4)$$

where

- t = minimum window thickness, in.
- P = pressure, lb/in.²
- r = radius of unsupported area, in.²
- S_a = allowable stress, lb/in.².

Circular flats of Irtran 1 and Irtran 2 were used in this work. Material failures were observed; Irtran 1 failed at 4538 atm and Irtran 2 failed at 5086 atm. The high-pressure cell may be used to 10 000 atm with suitable window material.

F. Measurements

The precise wave number of an absorption band center or peak maxima for liquid samples is obtained by static measurements, a more accurate technique.¹⁻³ The grating is positioned manually, and the output signal is read from the 0-100-mV digital voltmeter at each position of the grating.

Since the base plate of the monochromator is aluminum and the grating drive shaft is steel, any change in temperature of the monochromator rotates the grating by thermal expansion, without indication on the calibrated dial. Consequently, the temperature of the monochromator is read for each measurement and each dial reading is corrected to a reference temperature of 25°C.

The appropriate relationship between the wave number and the angular position of the grating is the grating equation; however, the following equation has been found satisfactory and convenient in this particular application where most measurements are within a short range of wavelengths. The wavenumber, which corresponds to a particular angular position of the grating, is given by,

$$\bar{\nu} = 10^4 / (k_1 + k_2 \bar{R}) \quad (5)$$

where, k_1 and k_2 = constants obtained from the calibration, \bar{R} = the temperature corrected dial reading, and k_2 is the slope of the linear function of the relationship between the wavelength and the grating position; i.e., it is a characteristic constant of the gear train and calibrated dial.

Millivolt readings from the potentiometer are equivalent to transmittances. Since the profile of absorption band of the liquid sample can be represented by Lorentz's formula,

$$\bar{T}(\bar{\nu}) = C_1 \exp\{-C_2 / [(\bar{\nu} - \bar{\nu}_0)^2 + \omega^2]\}, \quad (6)$$

where, $\bar{T}(\bar{\nu})$ and ω are the millivolt reading and the band half-width, respectively. In static measurements, readings are taken in the neighborhood of the peak maximum, $\bar{\nu}_0$; therefore, Eq. (6) can be expanded by a Taylor series and simplified to the following form:

$$\bar{T}(\bar{\nu}) = a + b(\bar{\nu} - \bar{\nu}_0)^2. \quad (7)$$

Table II. Preliminary shift data for *cis*-pentene-2 (at 25°C).

Pressure (atm)	State	Cell	$\bar{\nu}$ (cm ⁻¹)	$\Delta\bar{\nu} = \bar{\nu} - \bar{\nu}_0$ (cm ⁻¹)
≈ 0	gas		$\bar{\nu}_0 = 1667.312$	0.0
1.0	liquid	V.P. ^a ; I.P. ^b	1657.728	-9.484
10.0	...	I.P.	1656.741	-9.543
49.0	1657.677	-9.607
89.0	1657.475	-9.809
172.0	1657.495	-9.789
264.0	1657.361	-9.923
528.0	1657.560	-9.724
611.0	...	H.P. ^c	1657.671	-9.613
776.0	...	I.P. ^b	1657.665	-9.619
999.0	...	I.P. ^b	1658.135	-9.149
1024.0	...	H.P. ^c	1658.000	-9.284
1958.0	1658.622	-8.662
2942.0	1658.723	-8.561
3135.0	1658.371	-7.913
3658.0	1660.307	-6.977
4679.0	1660.388	-6.901
10.15 mole% <i>cis</i> -pentene-2 in carbon tetrachloride				
1.0	liquid	V.P. ^a	1656.591	-10.721
10.0	...	I.P. ^b	1656.740	-10.553
43.0	1656.534	-10.758
85.0	1656.809	-10.484
158.0	1656.618	-10.675
268.0	1656.534	-10.758
488.0	1656.446	-10.847
735.0	1656.382	-10.910
998.0	1656.360	-10.932

^a V.P. is variable path.

^b I.P. is intermediate pressure cell.

^c H.P. is high pressure cell.

Each reading of $\bar{T}(\bar{\nu})$ is taken at a fixed position of the grating, which is temperature corrected to \bar{R} . After a sequence of values of \bar{T} 's has been taken, they are fit to Eq. (7) by the least squares computer program, from which the accurate position of the band center, $\bar{\nu}_0$, is obtained; additional details are provided elsewhere.¹⁵

G. Experimental Measurements

Initial measurements using the techniques described were made using *cis*-pentene-2 and observing the C=C stretching frequency. Table II and Fig. 6 present some very preliminary data for pure *cis*-pentene-2 (spectrograde) and a mixture of approximately 10 mole% *cis*-pentene-2 in carbon tetrachloride solvent; the latter representing the case of the pentene molecules being essentially surrounded by CCl₄ molecules.

Preliminary error estimates for the modified spectrometer are (1) resolution, 0.5-1.0 cm⁻¹ (cf. IR5A ≥ 3.5 cm⁻¹); (2) precision of peak positioning, ± 0.001 cm⁻¹, and (3) shift precision ± 0.006 cm⁻¹. A typical value of shift, $\Delta\bar{\nu} = 9.149$ cm⁻¹, gives four significant figures with the uncertainty in the last figure.

The data are presented as a function of pressure which is the operating variable. Variation of the shift with volume is of primary interest and will be obtained as soon as the necessary PVT measurements have been completed.

ACKNOWLEDGMENT

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