

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 Fl58 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 | |
| RIR-20 | 5.5 | 1.82 at 2.2 μ | | 12-14 \times 10 ⁶ | | 760 | Insoluble |

^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, 1½ in. i.d. and 1¼ in. o.d. (No. 2-024), is used between two steel rings, and is expected to seal in the low pressure region (up to

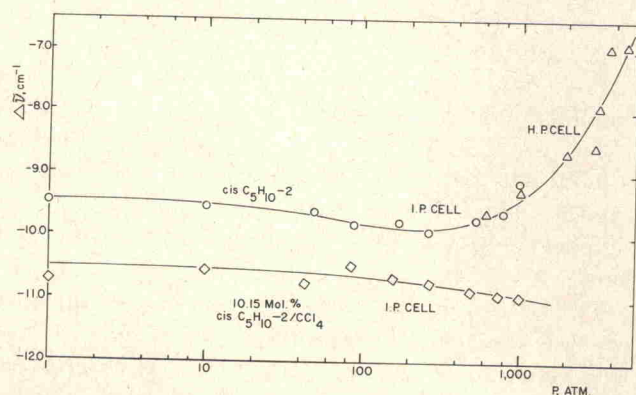


FIG. 6. Shifts of C=C vibration.

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 0.000 \pm 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. ^b | 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.