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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, servomoter, 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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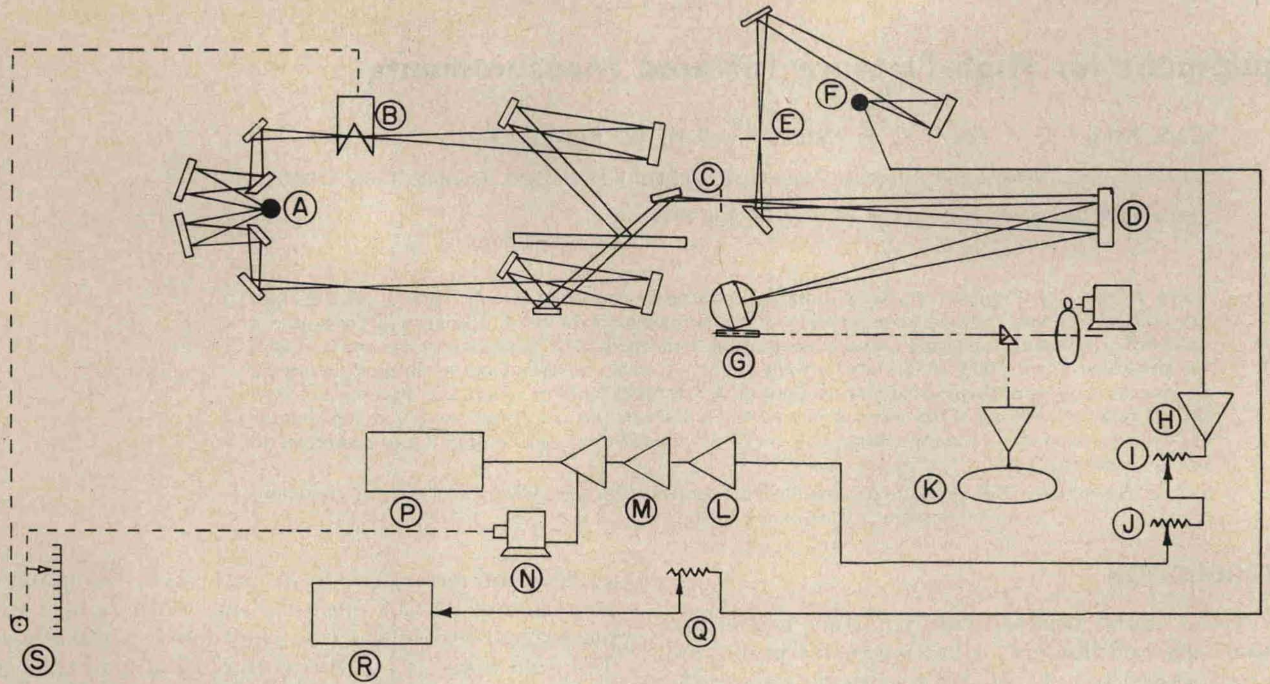

FIG. 1. Spectrophotometer diagram: (A) source; (B) comb; (C) entrance slit; (D) collimator; (E) exit slit; (F) detector; (G) grating; (H) preamplifier; (I) auxiliary gain; (J) gain; (K) calibrated dial; (L) voltage amplifier; (M) servoamplifier; (N) servomotor; (P) power supply; (Q) signal trimmer; (R)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

normal, the grating equation becomes

$$n\lambda = a(\sin\alpha + \sin\beta), \tag{1}$$

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 $n = 1, 2, 3, \cdots$. 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; there 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 wavelengths[5]; 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 cm^{-1}/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 and 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]