

Since the band position was independent of the time after compression, this condition was at least practically fulfilled. Furthermore, the experiments were carried out in an air conditioned room, in which the day-to-day temperature variation was small.

The details of the high-pressure apparatus are described elsewhere.<sup>8</sup> We present a schematic drawing, Fig. 1, to show the arrangement of low- and high-pressure ends, ring seals, and windows. The windows are similar to those used previously for high-pressure scintillation counting.<sup>9</sup> The use of sapphire windows limits this bomb to the spectral region between  $4\mu$  and  $0.2\mu$ . The high-pressure end was calibrated against the readings on a Bourdon gauge in the low-pressure end by means of a Manganin gauge. The gauge, not in place during spectroscopic runs, was inserted through the bottom plug. The pressures reported are considered accurate to  $\pm 25$  atmos.

The spectrometer used was a Perkin-Elmer Model 112. The external optics were replaced by an arrangement of two spherical mirrors allowing an image of the globar source to be focused on the sample in the bomb. Because of the  $\frac{1}{4}$ -inch hole at the end of the window plugs, there was still a considerable loss of radiation and it was found necessary to work at a fairly large slitwidth for this region (0.10 mm) and high gain. The resulting high noise level was partially smoothed by using a slow amplifier response and slow sweeping speed. Since we were interested in a small spectral region containing a single, intense band, no important errors were introduced by this procedure.

Most of the radiation path was swept clear of water vapor by a rapid flow of air from the laboratory supply line. The air was dried by  $\text{CaCl}_2$  and a liquid nitrogen trap. However, the 20 cm of exposed path in our present set up caused considerable absorption by the intense rotation-vibration band of water vapor in this region. Since we determined frequencies from the position of the absorption maximum, some error in the absolute values and in the frequency shifts was undoubtedly caused by the water vapor. In one case we performed a point-by-point subtraction of the water vapor band from the alcohol O-H band and found one or two wave number changes in  $\nu$  and in  $\Delta\nu$ . It was our feeling that the errors introduced by the subtraction procedure outweighed any gain in accuracy so obtained.

A LiF prism was used, calibrated by the rotational lines of the water vapor. Our estimate of the accuracy of frequency determinations, based on repeated observations, is  $\pm 2 \text{ cm}^{-1}$  in the value of  $\nu$  and  $\pm 1 \text{ cm}^{-1}$  in  $\Delta\nu$ .

#### EXPERIMENTAL RESULTS AND DISCUSSION

The data which we obtained are all presented in Table I. The results on *t*-butanol, 2% *n*-butanol, and

<sup>8</sup> E. Fishman and H. G. Drickamer, *Ind. and Eng. Chem.* (to be published).

<sup>9</sup> R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.* 21, 267 (1953).

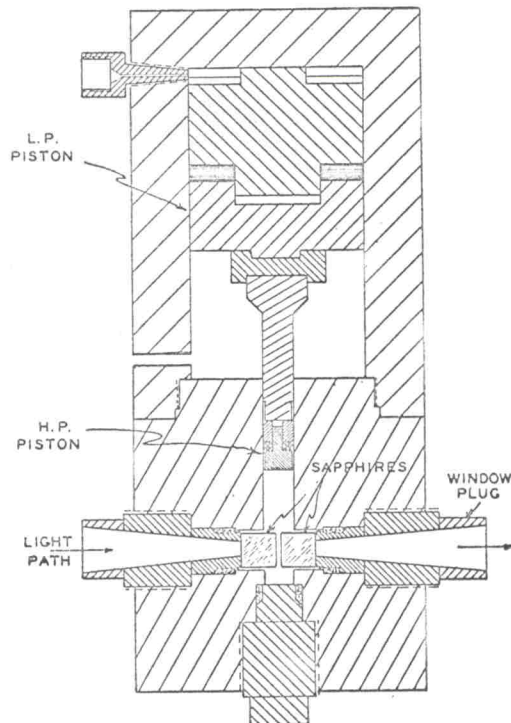


FIG. 1. Cross section of spectroscopic bomb.

methanol were obtained to determine the importance of the alkyl radical of the alcohol and the concentration on the frequency shifts. Comparison of these results with the *n*-BuOH in the same solvent show the existence of some effects due to the alkyl radical; however, they are not large and will be considered outside the scope of subsequent discussion.

There does not appear to be a record of the vapor phase spectrum of *n*-BuOH in the 3-micron region. The vapor phase spectrum of ethanol was reported with a central frequency of the O-H band at  $3640 \text{ cm}^{-1}$ ,<sup>10</sup> which ought to be close to the value for butanol. We find a frequency of  $3648 \text{ cm}^{-1}$  in 2, 3, DMB solution and this represents our best estimate of the O-H frequency in the unperturbed alcohol molecule. From the data in Table I, it is apparent that the greater the displacement of the O-H band from  $3648 \text{ cm}^{-1}$  at one atmosphere in a particular solvent, the greater is the pressure-induced shift. For subsequent discussion we denote  $\Delta\nu$  as the shift in frequency from its value at 1 atmosphere and  $25^\circ\text{C}$  for each solvent; therefore the values of  $\Delta\nu$  only indirectly reflect the difference in frequency in going from solvent to solvent, as indicated.

Since pressures of the order of 50 000 atmos are probably required to bring about significant compression of ordinary chemical bonds, it is clear that the frequency shifts reported are brought about by intermolecular effects, not by deformation of the molecules. Using

<sup>10</sup> J. Errera and P. Mollet, *Compt. rend.* 204, 259 (1937).