forces in solution by Benson and Drickamer (1957) is considered to apply here.

EXPERIMENTAL

The calcite used in this study was the Iceland Spar variety. It was obtained from Ward's Natural Science Establishment, Inc. Its high purity was established by an emission spectroscopic analysis.

All spectra were obtained on a Beckman IR-9 Infrared Spectrophotometer utilizing a 5X beam condenser equipped with potassium bromide lenses. Sample pressure was effected by means of a High Pressure Diamond Optics diamond-anvil cell equipped with type II diamonds. A rough pressure calibration was obtained with materials having well established transitions. Errors in pressure calculations exist due to inherent incapabilities of the cell. A uniform pressure cannot be applied to the sample due to an effect of concentrically-decreasing pressure at the diamond faces. This is to say that the highest pressure exerted will be at the center of the cell and decrease toward its outer edges.

The vaterite polymorph used in this study was synthesized by the method of McConnell (1959). An X-ray powder pattern confirmed the presence of vaterite in large quantities [minor amounts (10–15 percent) of calcite were also found].

X-ray patterns of the compressed calcium carbonate in the diamond cell at a pressure of 61 kbar was obtained by a flat camera with a sample to film distance of 45 mm using molybdenum radiation and exposed for eighteen hours. In that this work is an infrared study, the X-ray data was used only to supplement the infrared evidence of a high pressure polymorph.

RESULTS OF PRESSURE EFFECTS TO 60 KBAR ON THE SYMMETRY OF THE CARBONATE ION IN CALCITE

Pressure to approximately 30 kbars produces effects similar, though significantly different, to those observed by Weir, *et al.*, and Schock and Katz (1968) in experiments covering this pressure range. However, due to poor transmission of the diamond pressure cell in the ν_3 region (approximately 1400 cm^{-1}), confirmation of degeneracy of this mode was not attempted. The results of Weir, *et al.*, concerning this mode are plausible and have been accepted as valid.

A splitting of the doubly degenerate ν_4 mode is observed as pressure is increased. In view of the fact that weak bands are observed on both sides of this mode (approximately 715 cm^{-1}) at approximately 745 cm^{-1} and approximately 690 cm^{-1}, assignment of the degenerate components of this mode is formidable.

Schock and Katz assign the 714 cm^{-1} and 695 cm^{-1} bands as the components of the ν_4 split which results in a $\Delta\ \nu_4 \cong 19\ \text{cm}^{-1}$; a reasonable assumption. Weir, *et al.*, fail to observe the 695 cm^{-1} band and tentatively assign the ν_4 split to the 714 cm^{-1} and 740 cm^{-1} band. A larger $\Delta\ \nu_4$ ($\cong 26\ \text{cm}^{-1}$) results. Schock and Katz offer no assignment of the 740 cm^{-1} band and only note that it increases with pressure. We favor the degenerate split of the ν_4 mode at 714 cm^{-1} and 690 cm^{-1} for C_s site symmetry of aragonite and propose the 740 cm^{-1} band, which we also observe to increase with pressure, as being due to a change in the inplane bending constant indicative of repulsion between oxygen atoms in the plane of the carbonate ion. It should be noted that the effect of concentrically decreasing pressure inherent in the pressure cell can produce this change due to a mixture of polymorph species.

Due to the fact that the ν_4 fundamental is not a triple degenerate band it is believed to split due to a mixture of two polymorphic forms produced: one resulting in a 740 cm^{-1} band for an as yet unnamed polymorph and the other resulting in a 690 cm^{-1} band due to production of an aragonite polymorph. (The possibility of polymorphic mixtures due to uneven pressure has been previously described.) It has been observed that the 740 cm^{-1} band is the first to form; the 690 cm^{-1} band forms almost immediately after and remains stable, as we shall later show, under pressures from 25 kbar to 60 kbar. The 740 cm^{-1} band changes considerably under high pressure; this is to be expected if the causal interpretation of the band is correct.

The ν_1 fundamental is activated at high pressures and is reversible below 25 kbar in this work and that of Weir, *et al.* and is indicative of a deviation of the D_3 site symmetry rules. Schock and Katz found that for every specimen tested, 40 percent to 60 percent of the pressure induced absorption of the ν_1 fundamental remained upon release of pressure. The significance of these results will be discussed shortly.

It is our belief that the pressure induced changes in the fundamentals observed below 20 kbar are calcite I→II or II→III transitions, which many workers have suggested are metastable with respect to aragonite. The pressures of our transitions compare favorably with those proposed by Bridgman (1925): calcite I→II at 14.6 kbar and II→III at 17.7 kbar. Jamieson (1957) later demonstrated that as the pressure is increased calcite shows a diminuition in the intensities of the high-angle X-ray reflections and a decrease in the relative intensity of the $11\bar{2}3$ reflection. This phenomena was estimated to start at approximately 15 kbar. Between 20 kbar and 22 kbar, the $11\bar{2}3$ became extinguished, possibly indicating a halving of the *c*-axis. Their experimental evidence suggests that calcite II is an anion-disordered form of normal calcite.

Davis (1964) however, differs with the suggested mechanism of rota-