While the model experiments do not accurately reproduce geophysical conditions it is hoped that a careful experimental study will lead to the formulation of a theory which can then be extended to explain various aspects of auroral phenomena.

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<sup>1</sup> Quinn, R. G., and Chang, C. C., Trans. Amer. Geophys. Union, April (1965).

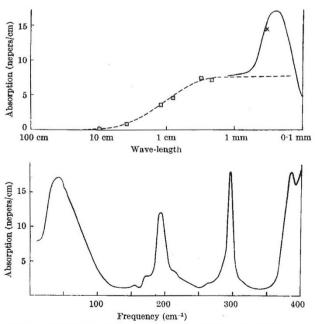
<sup>2</sup> Buneman, O., Phys. Rev., 115, 503 (1959).

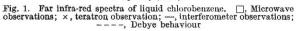
<sup>3</sup> Swift, D., J. Geophys. Res., 70, 3061 (1965).

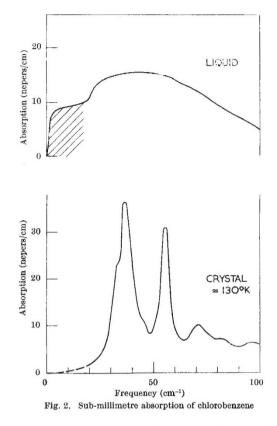
## Sub-millimetre Wave Spectra of Polar Liquids

In an earlier communication<sup>1</sup>, it was reported that liquid phase absorption of the monohalogenated benzenes at a frequency  $\approx 10^{12}$  c/s (1 teracycle) was higher than would be expected from the assumption that a simple Debye process was operative. The measurements supporting this conclusion were made using a CN maser source which gives only the single frequency 29.715 cm<sup>-1</sup> (337µ. wave-length). We have now supplemented these observations by wide-band spectral investigations using Fourier transform interferometric techniques.

The lower part of Fig. 1 shows results for chlorobenzene in the spectral range 10-400 cm<sup>-1</sup>. The sharp absorption features at 297 cm<sup>-1</sup> and 195 cm<sup>-1</sup> are known molecular vibration bands  $v_{24}$  ( $B_1$ ) and  $v_{50}$  ( $B_2$ ), respectively, and are the lowest frequency modes of the molecule<sup>2</sup>. However, the main interest here is the region below 100 cm<sup>-1</sup>, and in the upper part of Fig. 1 this region is plotted on a logarithmic frequency scale. The microwave observations are those of Poley<sup>3</sup> and that of Garg and Smyth<sup>4</sup>, and the interferometric measurements confirm the earlier maser observation. It can be seen that there is a broad but strong feature reaching a maximum at a frequency of 45 cm<sup>-1</sup> and that the peak is substantially greater than the asymptotic value to be expected at high frequencies from Debye's expression. These observations are believed to be the first reported of a complete band of this type though the high-frequency end of it is to be seen in the observations of Wyss et al.<sup>5</sup>. That such bands should exist is not surprising since they may be considered to arise from the







'pseudo-lattice' modes of the liquid, and for this there is support from the observations shown in Fig. 2. This shows the absorption spectrum of solid chlorobenzene at a temperature of  $\approx 130^{\circ}$  K with again the liquid spectrum (at room temperature) for comparison. The solid spectrum shows the relatively sharp features characteristic of a lattice spectrum, and it will be seen that these occur in the same frequency region as the diffuse band observed for the liquid. It should also be noted that the absorption in the region below 20 cm<sup>-1</sup> for the liquid (shown crosshatched) where Debye processes are dominant is absent in the solid, as is expected since it arises from the overall rotation of dipoles.

The exact nature of the pseudo-lattice in such liquids will be clarified by the results of further work, but the general picture of a polar molecule undergoing resonant oscillations in the force field of its immediate neighbours is acceptable. In such a model, the width of any absorption line would be determined by the lifetime of the pseudolattice state or, in other words, the reciprocal of the time over which the surrounding cage does not alter appreciably. This latter is the relaxation time, which is known from viscosity measurements or more directly from the frequency at which the Debye asymptote is nearly achieved. This is about 10 cm<sup>-1</sup> for chlorobenzene, and it is not hard to believe that the observed band is made up of a number of lines having widths of this order. The welldefined peak of the band is then explained by the reasonable assumption that the orientation of the oscillator in the 'cage' is not random, but has a most probable value which could be similar to that found in the crystal.

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<sup>4</sup> Garg, S. K., and Smyth, C. P., J. Chem. Phys., 42, 1397 (1965).
<sup>5</sup> Wyss, H. R., Werder, B. D., and Günthard, Hs. H., Spectrochim. Acta, 20, 573 (1964).