

some modification of the theory. Possibly consideration of the real field of the earth would provide a satisfactory interpretation of the situation. It may be noted that the latitude effect between the equator and 20°N for the voyage of the Millikan-Neher electroscope between Los Angeles and Melbourne was about 2.5 percent and if this is taken as a better value for comparison with the calculations based upon the equatorial asymmetry, both latitude and longitude effects demand the existence of an additional mixed component. On the other hand it must be borne in mind that certain corrections for diffusion of secondary radiations and for accidental counts are suggested as being applicable to the asymmetry measurements and these tend to raise the calculated latitude and longitude effects, so that it is quite possible that the positives alone can account for the whole of the field sensitive component.

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The Infrared Absorption Spectrum of Solid Hydrogen Chloride

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The infrared absorption spectrum of solid hydrogen chloride has been studied in the region of 3.7 μ with the aid of an echellette grating. The band is composed of a series of fairly broad lines, and if the center is taken to be the line at 2669 cm^{-1} the remaining lines taken in pairs can be grouped about this line with approximately equal spacings. Thus it appears that the band differs from the band in gaseous hydrogen chloride in that it has a zero line.

THE study of the absorption bands in the infrared of gas molecules under high dispersion has revealed many facts enabling one quite clearly to understand their behavior and structure. Many crystals show fully as well-developed bands as do gas molecules when measured with prism spectrometers, but only in few cases have measurements under high dispersion been made. Hardy and Silverman¹ and Silverman² have made measurements on quartz crystals and on the carbonates using an echellette grating and have found these bands to have a fine

structure far more complex than that of gas molecules. The bands may as in gas molecules be ascribed to vibrations of the atoms comprising the ionic configurations in the crystal lattice, but no mechanism adequately serves to explain the fine structure. Of the proposed explanations perhaps the most plausible is the theory that the ionic configurations may be thought of as rotating under certain constraints. Such theories have been advanced by chemists to explain specific heat curves for crystals. Attempts quantitatively to describe these phenomena have been made by Pauling,³ Stern⁴ and recently more

¹ Hardy and Silverman, *Phys. Rev.* **37**, 176 (1931).

² Silverman, *Phys. Rev.* **39**, 72 (1932); *Phys. Rev.* **45**, 158 (1934).

³ L. Pauling, *Phys. Rev.* **A36**, 430 (1930).

⁴ Stern, *Proc. Roy. Soc.* **130**, 551 (1930).

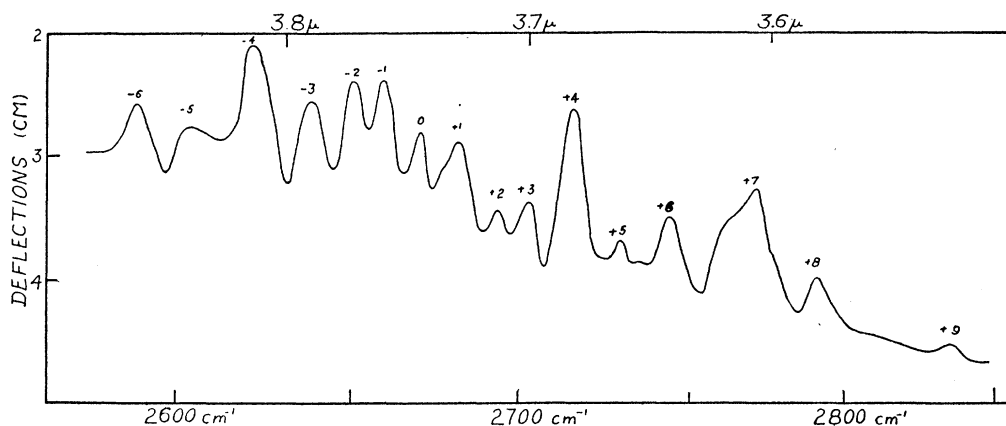


FIG. 1. Transmission curve of solid HCl—a composite of several runs.

completely by Nielsen.⁵ From the latter's work one sees that the rotational energy level scheme for a polyatomic configuration is so extremely complex that a theory of rotation might well account for the intricate absorption pattern found in quartz and in the carbonates.

In view of the extreme complexity of the energy level scheme for polyatomic molecules in crystals, it seems important to study the spectrum of a diatomic configuration where the scheme is much simpler. Hydrogen chloride in the solid form was chosen to work on since it had been pointed out by Pauling that rotation was here apt to take place; moreover, the preliminary work by Hettner⁶ on this substance had shown that the absorption at 3.7μ exhibited at least a doublet structure and gave a suggestion of a more complex structure.

For this experiment a vacuum system for manipulating the hydrogen chloride, equivalent except for unessential details to that used by Hettner, was constructed. To this system was sealed a Dewar flask of clear fused quartz from which the tip had been removed, so that by putting liquid air in the flask a thin layer of HCl could be frozen to the inside wall. The radiation was passed directly through the flask since liquid air is transparent to the spectral range here under investigation. The spectrograph was of a well-known design, fitted with a grating ruled with 800 lines per inch and used in fourth order. To

TABLE I. Wavelengths and frequencies of the lines in the 3.7μ band of solid HCl.

LINE NUMBER	FREQUENCY (cm ⁻¹)	WAVELENGTH IN μ	LINE NUMBER	FREQUENCY (cm ⁻¹)	WAVELENGTH IN μ
-6	2588	3.863	1	2681	3.729
-5	2606	3.837	2	2693	3.713
-4	2622	3.813	3	2703	3.700
-3	2639	3.791	4	2718	3.681
-2	2650	3.772	5	2729	3.664
-1	2660	3.760	6	2747	3.640
0	2669	3.746			

eliminate higher order radiation, a monochromatic device was inserted before the slit of the grating spectrometer. As experienced by Hettner, it was necessary to put the absorbing medium in the energy beam after dispersion rather than in the undispersed beam as is customary, since the total radiation absorbed by the 3.7μ region was sufficient to cause the absorbing layer to sublime to cooler regions of the flask.

The data were recorded in terms of galvanometer deflections for each circle setting. This seemed satisfactory since this region is quite free from atmospheric bands. The transmission curve, which is a composite over several runs, is shown in Fig. 1, circle settings having been replaced by a wavelength scale in μ and a frequency scale in cm⁻¹. As shown in Fig. 1, the absorption by solid hydrogen chloride is of a complex nature which has here been partly resolved. No claim of complete resolution is made since many of the lines appear broad and unsymmetrical and, moreover, because of considerable dissipation of

⁵ H. H. Nielsen, *J. Chem. Phys.* 3, 189 (1935).

⁶ G. Hettner, *Zeits. f. Physik* 78, 14 (1932).

light energy by scattering through the absorption chamber, rather wide spectrometer slits were necessary. Due to the constant boiling of the liquid air in the flask, the transmission of the light energy was not quite constant for a given setting so that the galvanometer deflections would fluctuate about some mean value determined by averaging over about ten readings. Consequently the actual relative intensities of the lines in the band must be considered doubtful. Because of rapidly increasing absorption toward longer wavelengths, the measurements were not carried beyond 3.9μ . In Table I are given the wavelengths and frequency positions of the lines as observed in the band.

It is here rather difficult to determine what is the center of the band. This can probably only be accomplished when an analysis of the line structure can be made, and it seems wiser to leave this to a later date when it is hoped more exact measurements can be completed. The line marked 0 is, however, chosen as the center because the other lines in the band, +1, -1, +2, -2, etc., taken in pairs occur almost equally spaced about it. If one adheres to a theory of rotation of the molecules, the rotation lines should form + and - branches and one would then expect corresponding lines in these branches to lie approximately the same distance from the center.

If this identification is assumed to be correct, this band in contrast to that of gaseous HCl has a 0 line. If the HCl molecule in the solid is assumed to be rotating under constraints, this is, however, not surprising, for if the molecule were completely clamped one can see from purely classical considerations that only the 0 line should occur. This may also be seen from Nielsen's work where for the electric moment along the axis of symmetry the selection rules are seen to be $\Delta v = \Delta k = \Delta n = 0$.

These measurements, which are really to be looked at as of a preliminary character, suggest very strongly that actual rotation of the HCl molecule in the solid state under certain constraints does take place. A new cell has been designed to eliminate the scattering of the light energy completely and where the light beam will not have to traverse the liquid-air medium. With it, it is hoped to repeat these readings with narrower slits and under more favorable conditions of observation.

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