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The values of the modified frequencies of radiation scattered by crystalline HCl and HBr at temperatures just below their freezing points are found to be 2784 cm^{-1} and 2480 cm^{-1}, respectively, for the long wave edge. As with gases and liquids, the intensities of scattering are in the reverse order of intensities of absorption and the difference in the Raman shifts with change of state is too great to be attributed to Lorentz-Lorenz forces alone.

The Raman band of crystalline HCl corresponds to the high frequency branch of two absorption bands found by Hettner, not to the center of the bands; on the possibility that, because of this correspondence, this branch is a Q-branch, the temperature variations of the absorption bands and the heat capacity at low temperatures can be accounted for. The non-existence of a third branch, for the R, is noted.

MODIFIED scattering by gaseous HCl has been reported by Wood[1] and Wood and Dieke,[2] by gaseous HBr and HI and liquid HCl and HBr by Salant and Sandow.[3] This paper is concerned with the modified scattering by crystalline HCl and HBr; the Raman shifts of the centers of these bands have already been recorded.[4]

APPARATUS AND EXPERIMENTAL RESULTS

A Hilger constant deviation spectrograph with the small camera (17 cm focus lens) having a dispersion of 356 cm^{-1}/mm at λ4550 was used, which, with the violet group of lines of a commercial six inch mercury arc (3 amp., 130 volts across the arc terminals) focussed into the crystals, gave Raman lines in half an hour and less with Eastman I–J plates.

The arrangement was the usual one according to Wood,—the cell, 6 cm$\times$1.5 cm diameter, being placed horizontally in a Dewar flask with a concave mirror on the side of the cell opposite the arc.

The scattered lines fall somewhat long of λ4358, in a region of considerable continuous background from the incident spectrum, which tends to obscure weak Raman lines. This continuous radiation and also the λ4358 group were

reduced greatly by a filter of 0.25 g of methyl violet in a liter of water, without reducing the intensities of $\lambda\lambda$4047 and 4078 appreciably.

HCl was prepared from NaCl and H$_2$SO$_4$, then dried in H$_2$SO$_4$ and condensed in the cell. HBr was generated by heating NaBr in syrupy H$_3$PO$_4$, then passed over red phosphorus, dried by CaCl$_2$ and P$_2$O$_5$ and passed through cooled traps into the cell. Perfectly clear crystals were obtained and kept several hours. The temperatures in the crystals were a few degrees below the freezing points. In attempted experiments with HI, dissociation occurred too rapidly to obtain lines.

Spectrograms and microphotometer curves of the Raman lines are reproduced in Figs. 1 and 2 respectively. In the latter is included a curve of a liquid HCl line obtained during these experiments, appearing much sharper than that previously reported,[3] though the two were microphotometered under identical conditions. The broadness of the earlier curve is attributed to continuous background, which is removed by the filter in the present experiments.

The lines, as may be seen from the curves, appear broad; the average values of the shifts of the edges from the parent lines being:

	Long wave edge vac. cm^{-1}	Short wave edge vac. cm^{-1}
HCl	2784$\pm$3	2743$\pm$4
HBr	2480$\pm$3	2449$\pm$4

These values were determined by a Hartmann interpolation formula using 24,705 and 24,516

[1] R. W. Wood, Phil. Mag. **7**, 744 (1929).
[2] R. W. Wood and G. H. Dieke, Phys. Rev. **36** 1355 (1930).
[3] E. O. Salant and A. Sandow, Phys. Rev. **37**, 373 (1931).
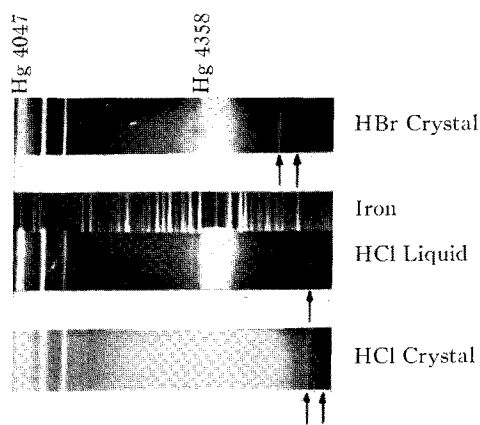[4] E. O. Salant and D. Callihan, Phys. Rev. **43**, 590 (1933).
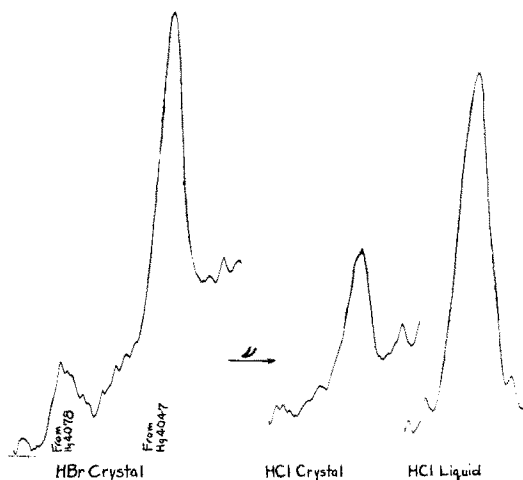
FIG. 1. Spectrograms of Raman lines.

FIG. 2. Microphotometric tracings of Raman lines.

cm^{-1} for $\lambda\lambda$4047 and 4078. As with the gas and liquid states, the order of intensities is HCl < HBr.

The separation of the two Raman lines (equal to the difference between $\lambda\lambda$4047 and 4078) on each spectrogram, is conclusive identification of the parent lines, so that the shift corresponds in order of magnitude to the $(1 \leftarrow 0)$ vibration of the molecules as given by Raman and infrared data[5] in the gaseous states.

The difference between the Raman frequencies of gaseous and solid HCl is too great to be entirely due to Lorentz-Lorenz forces, as calculated according to Breit and Salant.[6] The calculation gives approximately 3 cm^{-1} for HCl as

compared to the experimental value 102 cm^{-1}. The calculated value of the Lorentz-Lorenz displacement for HBr would be about the same as that of HCl and hence is much smaller than the 78 cm^{-1} measured result. A similar conclusion was drawn from comparison of gaseous and liquid data.[3]

The positive results obtained from these scattering experiments lend weight to the nature of the crystalline structure of the hydrogen halides as non-ionic, contrary to that given by Natta.[7]

DISCUSSION

It may be superfluous to remind the reader that the "Stokes" Raman band of a diatomic molecule is a Q branch and consequently the value of its high frequency edge (that is, the frequency difference between the exciting line and the long wave edge of the band as it appears on the plate) is the value of the $(1 \leftarrow 0)$ rotationless vibrational transition and that, consequently, this edge coincides with the center of the vibration-rotation band as it appears in absorption. This is seen clearly in the Raman bands of the gases of HCl and HBr.[1, 2, 3]

In Fig. 3 (a) are reproductions of absorption bands of crystalline HCl measured by Hettner[8] and of a microphotometric tracing of the Raman band of crystalline HCl measured by us. (There is no relation between their respective ordinates.) Surprisingly, the high frequency limit of the Raman band, 2784 cm^{-1}, agrees, not with the center of the two absorption bands, as would be expected if the two bands are P and R branches, but with the high frequency edge of the 2753 cm^{-1} band. It might be concluded that the 2753 cm^{-1} band is, accordingly, a Q and not an R branch; or, if the motions of the molecule transverse to its axis are vibratory rather than rotatory, that the 2784 cm^{-1} band represents the frequency ν_1 of motion along the axis and not the combination $\nu_1 + \nu_2$, where ν_2 is the frequency of motion transverse to the axis. (The band at 2712 cm^{-1} would be the P branch, or $\nu_1 - \nu_2$, on either interpretation of 2753.) But then the R branch, or $\nu_1 + \nu_2$, should appear at about 2856 cm^{-1}, and no such band is recorded by Hettner.

[5] C. F. Meyer and A. A. Levin, Phys. Rev. 34, 44 (1929); W. F. Colby, Phys. Rev. 34, 53 (1929).

[6] G. Breit and E. O. Salant, Phys. Rev. 36, 871 (1930).

[7] G. Natta, Nature 127, 235 (1931).

[8] G. Hettner, Zeits. f. Physik 78, 141 (1932).

Nevertheless, this interpretation does remove a number of difficulties. Hettner pointed out that at $T = 87°K$ the 2753 cm^{-1} band is less intense than the one at 2712 cm^{-1}, an impossible intensity relation if the bands are P and R branches; if the selection rules are modified (by the intermolecular fields) so as to permit Q transitions, the P branch may be expected to be the more intense. Furthermore, the relative weakness of the 2712 cm^{-1} band at $T = 20°K$, noted by Hettner, is to be expected if it is a P and the other a Q branch. Hettner noted that the frequency ν_2, obtained from regarding the 2753 cm^{-1} band as $\nu_1 + \nu_2$, led to impossibly large heat capacities at low temperatures. But if $\nu_1 = 2784$ cm^{-1}, then $\nu_2 = 72$ cm^{-1}, and the contributions of this motion to the molecular heat capacity at constant volume always lie below the values calculated by Clusius[9] from his experimental data for C_p, as they should. This appears in Fig. 4, where both $\frac{2}{3}$ Einstein and $\frac{2}{3}$ Debye heat capacity functions of $\theta = 103°$ ($\nu = 72$ cm^{-1}) are plotted ($\frac{2}{3}$ for two degrees of freedom). The close correspondence of the Debye curve with the measured heat capacities over a considerable range of lower temperatures is to be observed.[10]

In Fig. 3 (a) and (b) are shown reproductions of Hettner's curves at $T = 87°K$ and $T = 20°K$ drawn to the same scale. It is seen that, as the temperature is lowered, the maximum of the high frequency band shifts to *higher* frequencies, which it should if it is a Q branch, whereas it would shift to lower frequencies were it an R branch.

Thus, calling the quantum number governing the transverse motions of the molecule, j, and understanding that j may refer either to complete rotations or to pendulum motions of large or small amplitude, it would seem that, for this vibrational transition of HCl molecules in the crystalline state, $\Delta j \lesssim 0$, but that transitions $\Delta j > 0$ are forbidden. It is certainly not obvious how this is possible, but alternative suggestions

[9] K. Clusius, Zeits. f. physik. Chemie **B3**, 41 (1929).

[10] Below the transition point, $T = 98°K$, the heat capacity contributions due to a frequency of about 200 cm^{-1}, taken as a mean lattice frequency, give good agreement, when combined with the contributions of the transverse 72 cm^{-1}, with C_v values obtained from C_p data of Clusius by means of the Nernst-Lindemann $C_p - C_v$ formula.
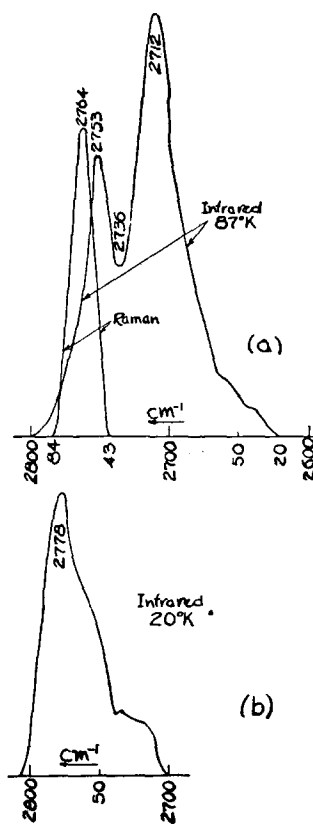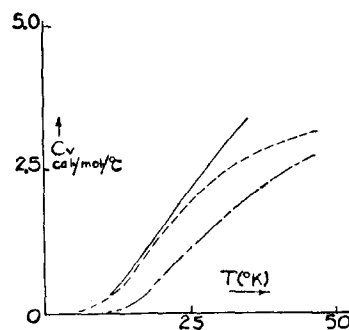

FIG. 3.

FIG. 4. Unbroken curve, experimental C_v; curve with even dashes, $C_v = \frac{2}{3}$ Debye function $\nu = 72$ cm^{-1}; curve with long and short dashes $C_v = \frac{2}{3}$ Einstein function $\nu = 72$ cm^{-1}.

considered to explain coincidence of the 2753 cm^{-1} absorption band and the Raman band gave impossible values of the heat capacity at low temperatures and the wrong behavior of the absorption bands with change of temperature.

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