

Infra-red and Raman Spectra of Crystalline Hydrochloric Acid

A KNOWLEDGE of the vibration-rotation spectra of crystalline hydrochloric acid is of considerable importance in view of the theories of Pauling¹, Fowler², and others on rotation in the solid state. Although several investigators have taken up this problem, the existing experimental data are confusing and even conflicting. Thus Hettner³ has reported that in infra-red absorption a doublet band is found below the transition point (98° K.) and a single absorption maximum above it. On the other hand, Shearin⁴ has reported the existence of thirteen discrete rotation lines at liquid air temperature (that is, around 85° K.) and this result has recently been quoted⁵ as indicating that rotation exists below the transition point. It seemed possible that the discrepancy between those two results might be due to the fact that Shearin had the higher resolving power of a grating at his disposal. We have just completed a very careful examination of the absorption near 3.7μ of thin layers of solid hydrochloric acid at the temperature of liquid air, using a grating spectrometer at least equal to that of Shearin's in resolving power.

Our observations agree very closely with those of Hettner for this temperature. We can find no trace of the individual lines in the positions indicated by Shearin, although there are signs of some further structure in the doublet. In addition, we have examined the absorption of layers of solid DCl near 5μ at the same temperature. Here we find not two peaks but three distinct maxima with indications of more structure. The two extreme maxima appear to correspond to the maxima of the HCl doublet, since their frequencies give the same isotopic ratio. As regards the appearance of the third maximum, we might remark that we have had indications of a similar additional peak in HCl when the gas has been condensed on to a surface at a temperature above that of liquid air and afterwards cooled to liquid air temperature. The pure doublet is obtained when the hydrochloric acid is condensed immediately on a surface at liquid air temperature.

VIBRATION SPECTRA OF CRYSTALLINE HYDROCHLORIC ACID

| | Observers' initials | Below transition point | Above transition point | DCl |
|----------------------|---------------------|------------------------|------------------------|--|
| Infra-red absorption | H. | 2708(s)2747(w) | 2768 | $\left\{ \begin{array}{l} 1990(w) \\ 1979(m) \\ 1965(s) \end{array} \right.$ |
| | L.S. & W. | 2704(s)2746(w) | | |
| Raman scattering | C. & S. | | 2763 | |
| | L.S. & W. | 2709(s)2759(w) | | |

s=strong, m=medium, w=weak in intensity.

The only observations on the Raman spectrum of solid hydrochloric acid are those of Callihan and Salant⁵, who found a single broad line extending from 2,743 cm^{-1} to 2,784 cm^{-1} . The centre of this line is in good agreement with the centre of the single absorption peak found by Hettner above the transition point at 100° K. Since the scattering experiments were done with the crystal only a few degrees below the melting point (presumably about 155° K.) this seems quite satisfactory. We have now succeeded in observing the Raman spectrum of hydrochloric acid at the temperature of liquid air. We find that it consists of two distinct lines, one of which, lying at 2,709 cm^{-1} , is much stronger and broader than

the other at 2,759 cm^{-1} . The uncertainty in the determination of the Raman frequencies is unlikely to be greater than 5 cm^{-1} , and of the infra-red ones, 2 cm^{-1} , so there appears to be a small discrepancy between the value of the higher frequency according as it is observed in absorption or in scattering.

A full account of these experiments, which are being continued at other temperatures and on methane and germane, will appear later elsewhere.

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¹ Pauling, *Phys. Rev.*, **43**, 430 (1930); Fowler, R. H., *Proc. Roy. Soc.*, **A**, **149**, 1 (1935).

² Hettner, *Z. Phys.*, **89**, 234 (1934).

³ Shearin, *Phys. Rev.*, **48**, 299 (1935).

⁴ Bartholomé, Drikos and Eucken, *Z. phys. Chem.*, **B**, **39**, 371 (1938).

⁵ Callihan and Salant, *J. Chem. Phys.*, **2**, 317 (1934).

Predissociation Phenomena in Spectra of some Diatomic Molecules

IN emission at low pressure, the *C*-band (0,0) of strontium hydride is cut off above $R(18) = 26,549 \text{ cm}^{-1}$, the upper level of which (*C*, $v = 0$, $J = 19$) lies 27,776 cm^{-1} above the ground-level *N*, $v = 0$, $J = 0$. In spite of this, Watson and co-workers found no traces of the (1,0) band in emission at low pressure, though the levels *C*, $v = 1$, $J = 1$ to $J = 6$ lie only 27,620 to 27,770 cm^{-1} above this ground-level (cf. More and Cornell¹, table 1). Thus the statement of More and Cornell (p. 808) that the (1,0) band "lies far beyond the predissociation limit at $K' = 19$ in the (0,0) band" must be incorrect. Consequently the predissociation occurs at an energy-level at least $\sim 150 \text{ cm}^{-1}$ lower in *C*, $v = 1$ than in $v = 0$. Previously Herzberg² has found similar cases in the P_2 and N_2 molecules.

Now it is very interesting that the *C* state of barium hydride behaves in quite an opposite way³. Here in emission the (1,1) band is clearly present, while only very faint traces can be recovered of the (0,0) band. Apparently we have to deal with two different cases of predissociation: in the first case (P_2 , N_2 , CO, SrH . . .) the cut-off appears at lower energy and of course at lower *J*-value, in a higher vibrational level than in a lower *J*; in the second case (BaH), the cut-off occurs at lower energy in a lower vibrational level than in a higher.

According to Herzberg, the first case of predissociation here mentioned may be explained as an effect of potential barriers at large nuclear distances in the intersecting potential curve (Herzberg, case b). But if the "crossing over" occurs above the predissociation limit (Herzberg, case c), the transitions between the predissociated and intersecting potential curves take a greater role in the predissociation phenomena than in the first case mentioned. According to the Frank-Condon principle, the two cases of predissociation then may be explained as an effect of overlapping wave functions. In $v = 0$ of the predissociated state, the wave function has one maximum between the turning points. In the higher vibrational levels the maxima at the turning points are larger than those between the points. Further, the difference $r_{\text{max}} - r_{\text{min}}$ between the turning points is larger at the same energy in a higher vibrational level with a lower *J* value, than in a lower vibrational