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I. THE INFRARED SPECTRUM AND THE STRUCTURE OF THE LOW TEMPERATURE PHASES OF CRYSTALLINE HCl, HBr, AND HI

By

D. F. Hornig and W. E. Osberg

II. INFRARED SPECTRA AND STRUCTURE OF CRYSTALLINE AMMONIA HYDRATES

By

R. D. Waldron and D. F. Hornig

Metcalf Research Laboratory
Brown University
Providence, Rhode Island

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ABSTRACT

The infrared spectra of crystalline HCl, HBr and HI have been studied at -205°C. The fundamental vibration was observed in HCL at 2704 and 2746 cm^{-1}, in HBr at 2404 and 2438 cm^{-1}, and in HI at 2120 cm-1. In addition, low frequency bands associated with torsional lattice vibrations were observed directly and in combination with the fundamental vibration of the molecules. It is concluded that in the low temperature crystalline phase both HCl and HBr form zig-zag hydrogen bonded chains, the angle between adjacent molecules being about 107° in HCl and 97° in HBr. The crystalline potential function is investigated for all three molecules.

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INTRODUCTION

Although the position of the halogen atoms in the lowest temperature phase of the hydrogen halides has been measured by X-ray methods, and the determination is probably fairly reliable in the case of hydrogen chloride, the position of the hydrogen atoms, upon which many of the physical properties of these crystals depend, is unknown. Until more is known of the structure of the lowest temperature phase there is little hope of understanding the structural principles on which these simple crystals are constructed or the nature of the solid state phase transitions which occur in HCl, HBr and HI.

These transitions are probably connected with the reorientation and disordering of the molecules, but although they have been studied by thermodynamic, optical, spectroscopic, X-ray and dielectric techniques, the nature of the structural changes is not understood. Much of the information (prior to 1938) concerning these transitions is summarized in a review by Eucken.[1] However, it is clear from the previous infrared studies[2,3]

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[1] A. Eucken, Z. Elektrochem. 45, 126 (1939)

[2] G. Hettner, Z. Physik, 78, 141 (1932); ibid. 89, 234 (1934); Ann. Physik (5), 32, 141 (1938)

[3] Lee, Sutherland & Wu, Nature, 142 669 (1938); Proc. Roy. Soc. (London), A176, 493 (1940)

and the more recent nuclear magnetic resonance experiments[4] that there is no free or nearly free molecular rotation in any of the phases.

Most recent theoretical discussions of the structures and the phase transitions are based on models consisting of dipole arrays. Since the intermolecular distance is not much greater than the interatomic distance in a single molecule, there is a real question as to whether such models are applicable. In any case, Luttinger and Tisza[5] have predicted on the basis of such a model that the lowest temperature ordered phase consists of antiparallel strings of dipoles, and this can be checked from the infrared spectrum.

Since these molecules have but a single internal mode of vibration there should be little ambiguity in the interpretation of the infrared spectrum in terms of the present theory of molecular vibrations in crystals[6]. A completely unambiguous determination of the crystal structure is out of the question but certain features of the structure can certainly be obtained. For example, it should be possible to decide whether or not the structure is ordered; and if it is ordered to gain some knowledge of the number and arrangement of the molecules in a unit cell from the *number* of absorption peaks associated with the single mode of vibration. The orientation of the molecules should be revealed by the relative *intensity* of these

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[4] N. L. Alpert, Phys. Rev. 75, 398 (1949)

[5] J. M. Luttinger and L. Tisza, Phys. Rev. 70, 954 (1946)

[6] D. F. Hornig, J. Chem. Phys. 16, 1063 (1948)

coupling components. In addition a quantitative measure of the intermolecular forces should be available from (a) the change in the mean internal frequency in passing from gas to crystal (b) the magnitude of the separation between coupling components (c) the magnitude of the torsional oscillation frequency in the crystal (which has not been observed heretofore).

The infrared spectra of crystalline HCl, HBr and HI have all been studied before[2,3,7] although HBr and HI were not obtained in the lowest temperature phase, which exists below 89°K and 70°K respectively. The spectrum of thin films of HCl has been studied between 1.5μ and 4.15μ and the existence of two distant peaks at about 2705 cm^{-1} and 2746 cm^{-1} noted in the low temperature phase (i.e. below 98.4°K).[2,3] Since the completion of the work reported here the infrared spectrum of a dilute solution of HCl in crystalline DCl has led to the conclusion that the angle between adjacent hydrogen bonded HCl molecules is either 102° or 78° [8], contrary to the theoretical expectations. The Raman spectrum of HCl has also been studied[2,9], and two peaks observed in the low temperature phase[2], only one of them coinciding in frequency with an infrared absorption maximum to within the combined experimental error.

However, no satisfactory interpretation of these observations has been evolved.

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7. J. Zunino, Zeits. f. Phys. <u>100</u>, 335 (1936)

8. G. L. Hiebert and D. F. Hornig, J. Chem, Phys. <u>20</u>, 918 (1952)

9. D. Callihan and E. O. Salant, J. Chem. Phys. <u>2</u>, 317 (1934)

Experimental Techniques

Two different samples of hydrogen chloride were used in this work, commercial hydrogen chloride whose purity was stated to be 99.5%, the impurities consisting of 0.2% acetylene and 0.3% chlorinated hydrocarbon, and a sample prepared from reagent grade sodium chloride plus sulfuric acid. The first sample was used without further purification; the second was dried over anhydrous aluminum chloride and collected at liquid nitrogen temperature. The spectra obtained from the two samples were identical.

Commercial hydrogen bromide* was used without further purification. The purity of the material was reported as 99.5%, the gas containing no bromine or moisture; the principal impurity was nitrogen.

Hydrogen iodide was prepared by adding sodium iodide to phosphoric acid at dry ice temperature, sealing and evacuating the system, and then allowing the mixture to warm until reaction took place. The gas was passed through a trap at -35°C to remove water or iodine and collected as a solid in a trap at liquid nitrogen temperature. The entire system was wrapped in aluminum foil to prevent the photodecomposition which occurred when this precaution was not taken.

The spectra were studied in the low temperature sample cell shown in Figs. 1a and 1b.[10] It is similar to that described previously[11] except for the additional sidearm I through which the sample was sublimed onto the plate B, and the provision

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* The Matheson Company, Inc.

[10] J. B. Lohman, Ph. D Thesis, Brown University, 1951.

[11] E. L. Wagner and D. F. Hornig, J. Chem. Phys. 18, 296 (1950)

FIG. 1A

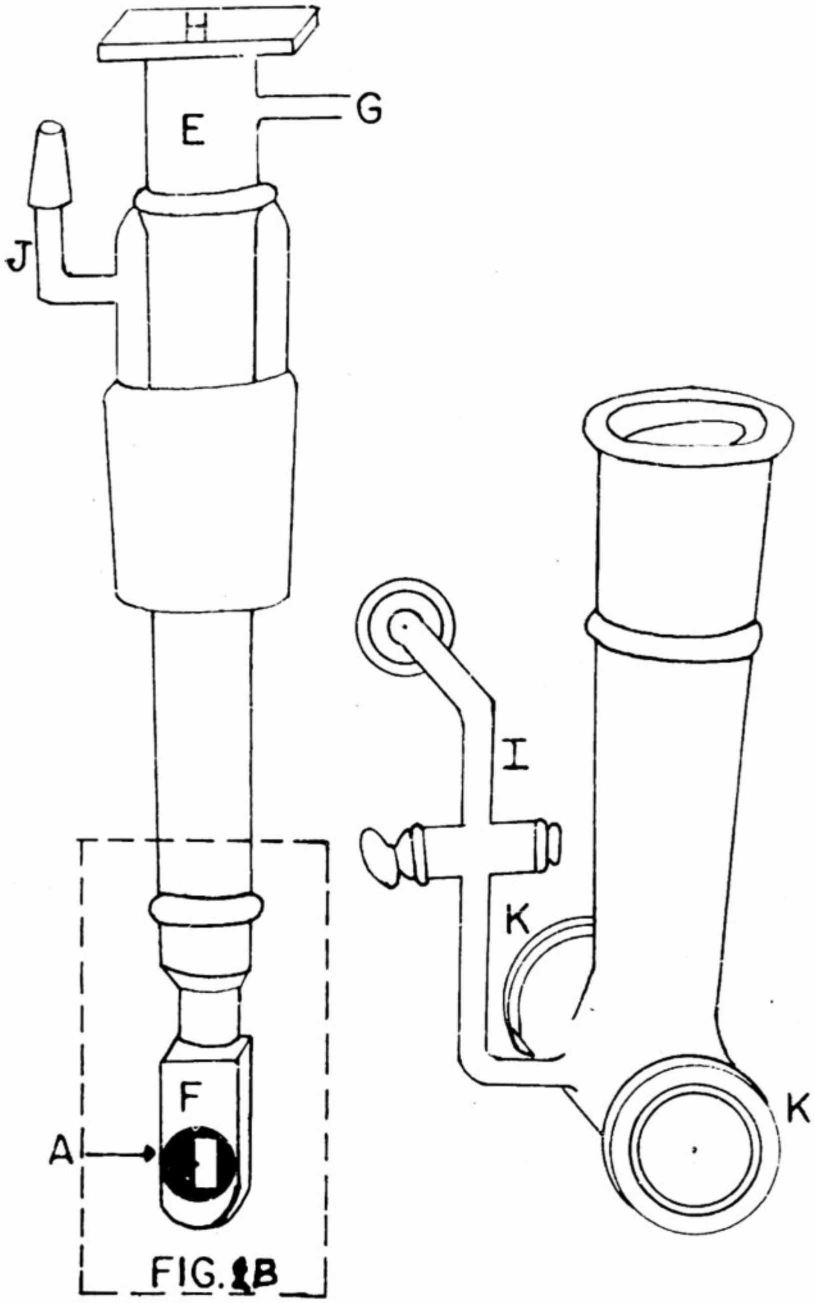
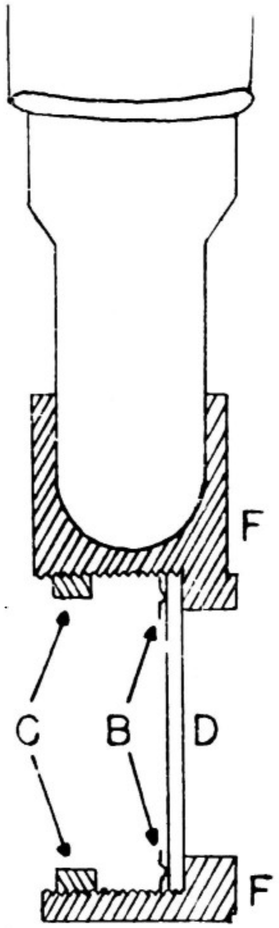


FIG. 1B



which was made for cooling the liquid nitrogen to the triple point by pumping through the sidearm G. The sample was mounted on window D which was held in good thermal contact with the copper block F at all times during the cooling process by a spring B and a retaining ring C which was screwed firmly into place. With this simple arrangement the temperature difference between window and block, measured by inserting a thermocouple into a small hole drilled in the window, did not exceed 3°C when the block was at the temperature of liquid nitrogen.

The plastic plate H simply rested on the chimney E above the liquid nitrogen reservoir, and produced an adequate seal when pumping on G. In order to replenish the liquid nitrogen, the plate H was removed without disconnecting the pump, liquid nitrogen added to E, and the plate replaced. No detectable fluctuation was observed in the temperature of the block F during this process, which could be carried out rapidly. The temperature of the block was measured by a thermocouple whose leads were passed through a seal which was attached to the ground glass joint J.

The films were prepared by first condensing the gas in a trap attached to I, cooling the cell to approximately the triple point of nitrogen (-210° C.) and then lowering the liquid nitrogen from around the trap by such an amount as to sublime the material at a vapor pressure of about 5 mm. Hg to the cooled plate D. Of course a large part of the material actually condensed on the brass block F but this was of no consequence. After the film was deposited the jacket was reevacuated with a diffusion pump to minimize the heat loss to the outer walls.

Early in the investigation it was found that thin films of HCl and HBr evaporated rapidly from the window at liquid nitrogen temperature (-195°C) but could be retained if the temperature were lowered to the triple point of nitrogen (-210°C).

The films prepared by this technique were quite transparent to the eye and showed little or no scattering of the infrared radiation.

The spectra of the films were studied from 300 cm^{-1} to 4000 cm^{-1} with a double beam spectrophotometer[12], the low temperature cell being in one path and an evacuated cell of the same length with similar windows in the other. The spectrometer housing was flushed with dry nitrogen to remove CO_2 and H_2O but in the spectra of some of the HBr films there is evidence that the flushing may not have been equally efficient in both beams. Stray radiation in the KBr region was eliminated by a scattering filter and that in the KRS-5 region minimized by replacing the mirror before the entrance slit with a stainless steel mirror, roughened by grinding with Aluminox No. 120. Nevertheless, 31% of the total radiation at 310 cm^{-1} was transmitted by an NaCl plate and was therefore stray. It should be noted that the low frequency limit of the spectral region investigated was determined by the transmission of the thin KBr window on the thermocouple.

The spectrometer calibration was checked against atmospheric water and CO_2 bands. The frequencies reported are believed to be accurate to ± 3 cm^{-1} at 2700 cm^{-1}, 1.5 cm^{-1} at 2100 cm^{-1} and better than 1 cm^{-1} in the low frequency region.

Experimental Results

a. Hydrogen Chloride

The spectra obtained at a temperature of 73°K., well below the temperature of the phase transition at 98.8°K., with the film on a KBr backing, is shown in Figure 2. A film of HCl deposited on NaCl to check the effect of the substrate yielded a similar spectrum, although the intensity of the two peaks was more nearly equal.

The spectrum of thin films, (Fig. 2) in good agreement with the high resolution

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[12] Hornig, Hyde and Adcock, J. Opt. Soc. Am., 40, 497 (1950)

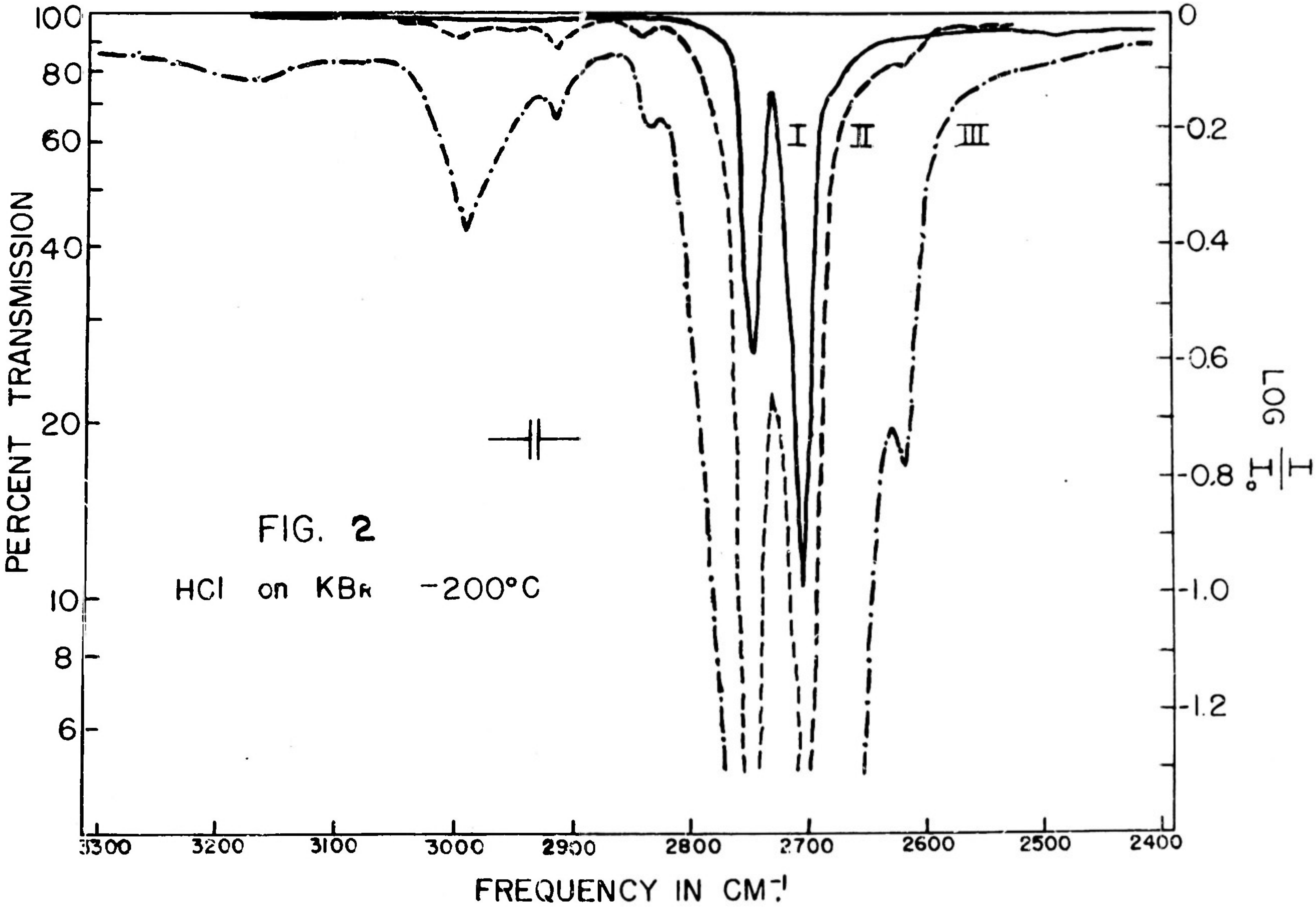

FIG. 2

HCl on KBr −200°C

study of Lee, Wu and Sutherland who found maxima at 2701 cm^{-1} and 2744 cm^{-1}, consists of two sharp lines at 2704 ± 3 cm^{-1} and 2746 ± 3 cm^{-1}, whose widths at half peak intensity are approximately 30 cm^{-1}. The spectra of thick films show a number of previously unreported regions of absorption, a sharp line at 2616 ± 3 cm^{-1}, a somewhat weaker band at 2991 cm^{-1} whose width is roughly 50 cm^{-1}, and a very weak band at 3171 cm^{-1}. Two other peaks, at 2837 cm^{-1} and 2916 cm^{-1}, are believed to originate in Apiezon-M stopcock grease which was carried into the cell from the vacuum system with the HCl. They occur in the spectrum of Apiezon-M and were not found in other HCl spectra taken when a fluorocarbon grease (DuPont FXC-441) was used as a stopcock lubricant.

A very thick film (Fig. 3) also showed absorption maxima at 315 cm^{-1}, 496 cm^{-1} and roughly 650 cm^{-1}. The true maximum of the lowest frequency peak may be at a still lower frequency since it occurs just at the limit of our measurements, where stray radiation is a very serious problem. The width of the 496 cm^{-1} line is about 55 cm^{-1} and of the 650 cm^{-1} line about 75 cm^{-1}.

The two strong sharp lines are certainly coupling components of the fundamental stretching vibration. The origin of the sharp weak line at 2616 cm^{-1} is doubtful. Although it may be a third component of the stretching vibration, there are strong reasons to believe this is not the case. It might be a difference vibration involving a lattice frequency of about 100 cm^{-1} but the corresponding sum is absent. If it is caused by an impurity it is not easy to find any reasonable possibilities. The intensity of the peak is about the same in the spectrum of HCl from different sources. The most likely impurity is the OH_3^+ ion resulting from traces of H_2O, perhaps absorbed on the KBr or NaCl. A broad absorption maximum has been observed recently at 2600 cm^{-1} in the compound OH_3Cl[13];

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[13] C. C. Ferriso and D. F. Hornig, J. Am. Chem. Soc. 75, 4113 (1953)

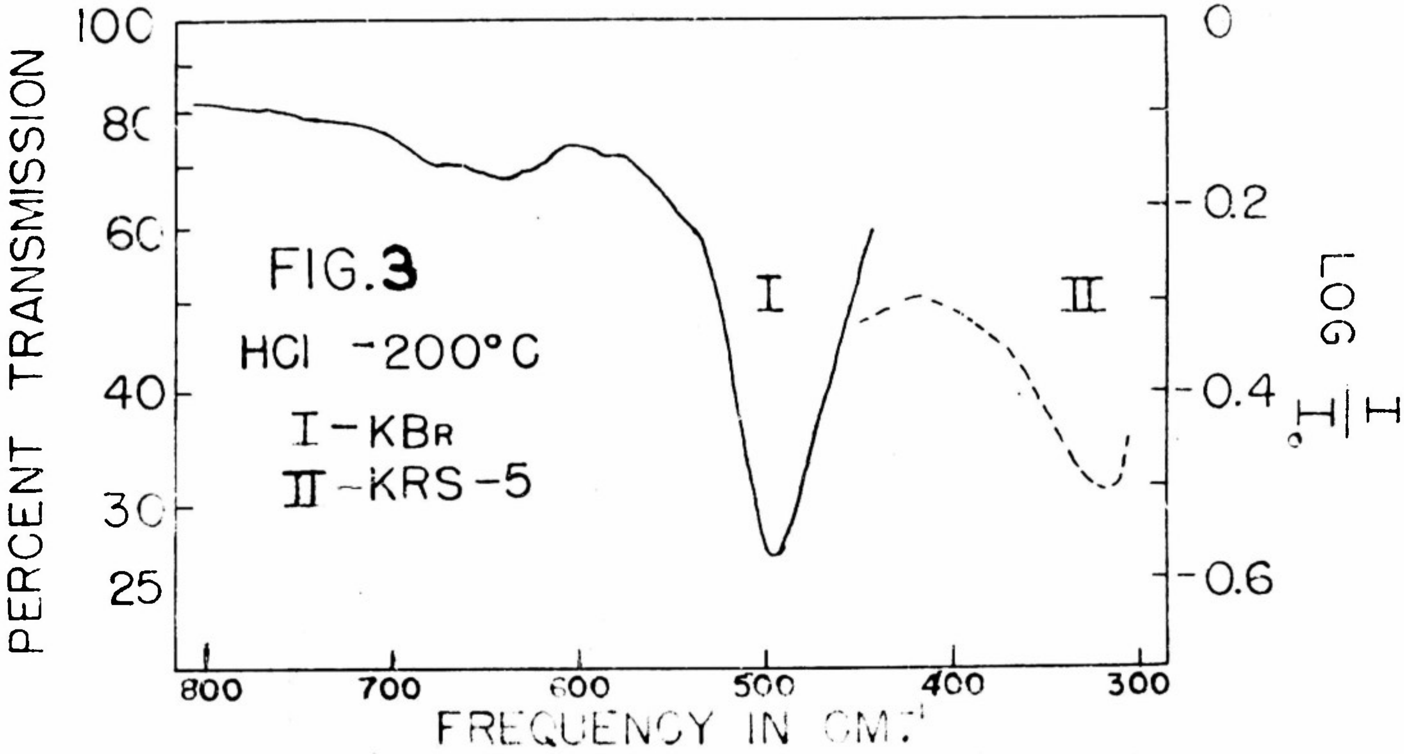100
80
60
40
30
25
PERCENT TRANSMISSION
0
-0.2
-0.4
-0.6
LOG $\frac{I}{I_0}$
800
700
600
500
400
300
FREQUENCY IN CM.$^{-1}$
I
II
HCl -200°C
I - KBr
II - KRS-5

FIG.3

however, subsequent studies of dilute solutions of H_2O in crystalline HCl[14] did not disclose a corresponding sharp line, nor is a corresponding peak found in our spectra of HBr, although the maximum at 2600 cm^{-1} was also found in OH_3Br.

Nevertheless, it is our opinion that the weak line at 2616 cm^{-1} is not to be ascribed to a fundamental vibration for the following reasons, some of which are elaborated later:

(a) No corresponding line has been found in recent studies of thick films of DCl.[15]

(b) Sutherland found a Raman line at 2709 ± 5 cm^{-1} and an infrared line at 2701 ± 1 cm^{-1}. Unless they actually coincide, no assignment is available for the line in question.

(c) The existence of a component at 2616 cm^{-1} would imply strong coupling between each HCl molecule and one neighbor in addition to the one to which it is hydrogen bonded. If this were the case, two different sets of "wings" should have been obtained in the spectra of dilute solutions of HCl in DCl. The second set, which would be separated by about 22 cm^{-1} from the main peak, was not observed.

(d) The existence of a coupling component at a frequency as low as 2616 cm^{-1} would imply a spread of over 100 cm^{-1} in the broad band in the disordered phase above 98.8°K. In fact, the spread of the band is about 50 cm^{-1}, about equal to the separation of the two Raman peaks and the two infrared maxima[2].

In the subsequent discussion it will be assumed that the peak at 2616 cm^{-1} cannot be ascribed to a fundamental vibration. However, the changes in the reasoning which are necessary if it is will be pointed out explicitly.

The frequencies 496 cm^{-1} and 650 cm^{-1} cannot be the fundamental lattice torsions since they could be expected to be very intense, even more so than in NH_3 where the

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[14] C. C. Ferriso, unpublished work

[15] G. L. Hiebert, unpublished work

torsion is the strongest band in the spectrum[16], while these were observed only in thick films. They are probably overtones or combinations of still lower frequency lattice modes. The broad peaks at 2991 cm^{-1} and 3171 cm^{-1} are probably combinations of the stretching vibration with lattice frequencies (probably largely torsional) near 266 cm^{-1} and 446 cm^{-1} respectively. The latter may be some of the same levels which give rise to the 496 cm^{-1} band.

b. Hydrogen Bromide.

Hydrogen bromide was studied on KBr, NaCl and CaF$_2$ backing plates. The transmission curves obtained for the lowest temperature phase on KBr are reproduced in Figs. 4 and 5. The temperature of the films (73°K.) was well below the transition temperature, 39°K. The spectra of thin films closely resemble the corresponding spectra of hydrogen chloride, showing two sharp lines at 2404±3 cm^{-1} and 2438±4 cm^{-1}, in contrast to the single broad band centered at 2420 cm^{-1} reported by Zunino for the crystal at 88°K. It is apparent that Zunino's crystal was not in the lowest temperature phase. The two bands are quite narrow, their widths at half peak intensity being 25 cm^{-1} and 20 cm^{-1} respectively.

The spectra of very thick films show another sharp line (approximately 20 cm^{-1} wide) at 2727 cm^{-1}, which may be analogous to the high frequency band in hydrogen chloride. This band appears to be much stronger in the non-scattering film on CaF$_2$ than in the highly scattering film on KBr, but since it is not at all certain that the absorption in other peaks by the scattering film is as great either, it may actually have been a thinner specimen. This apparent intensity variation might also be taken as evidence of orientation on KBr, together with a high degree of polarizatio of the band. However, it seems most likely that this line arises because of traces

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[16] F. P. Reding and D. F. Hornig, J. Chem. Phys. 19, 594 (1951)

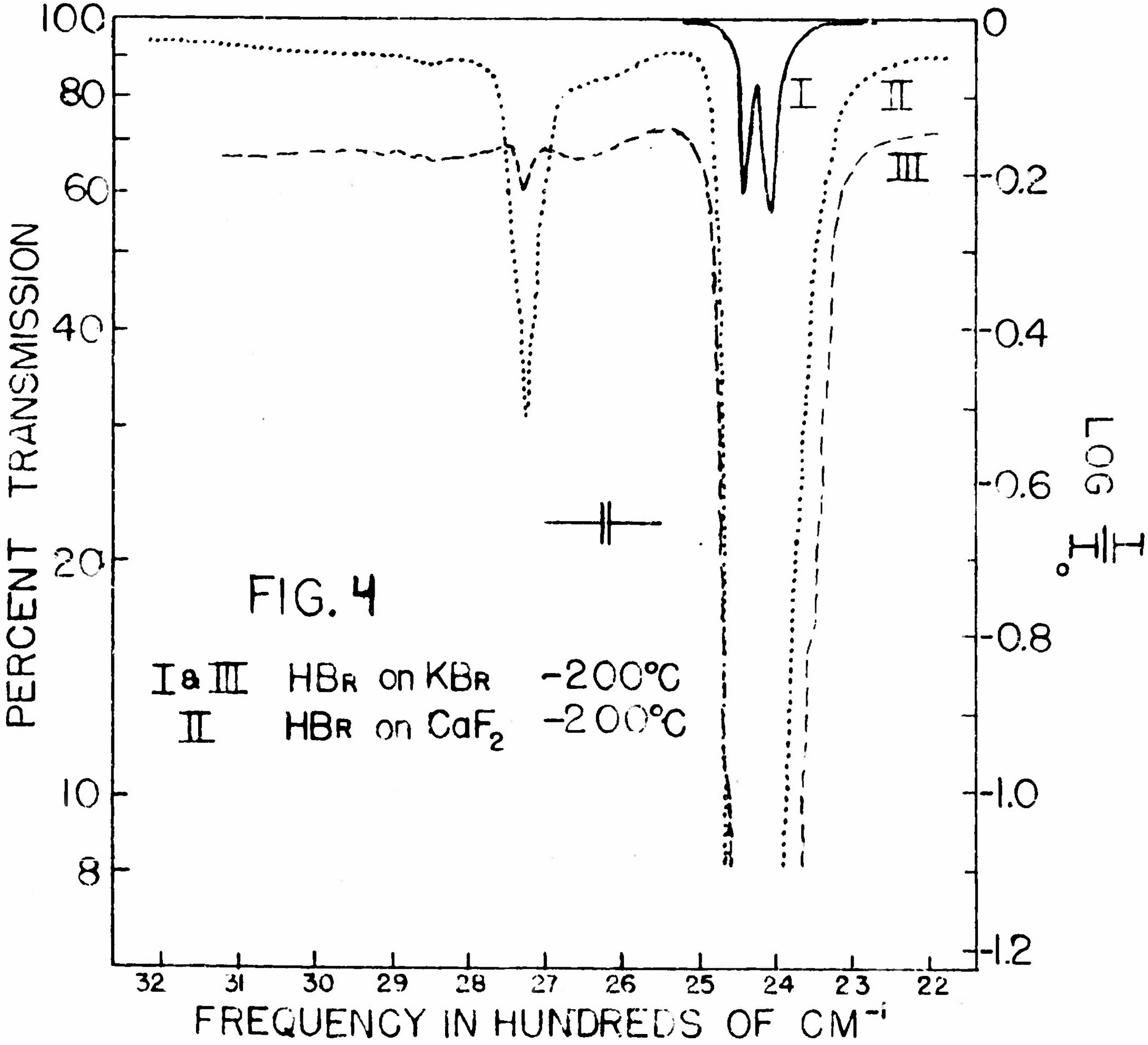

FIG. 4

I & III HBr on KBr −200°C
II HBr on CaF$_2$ −200°C

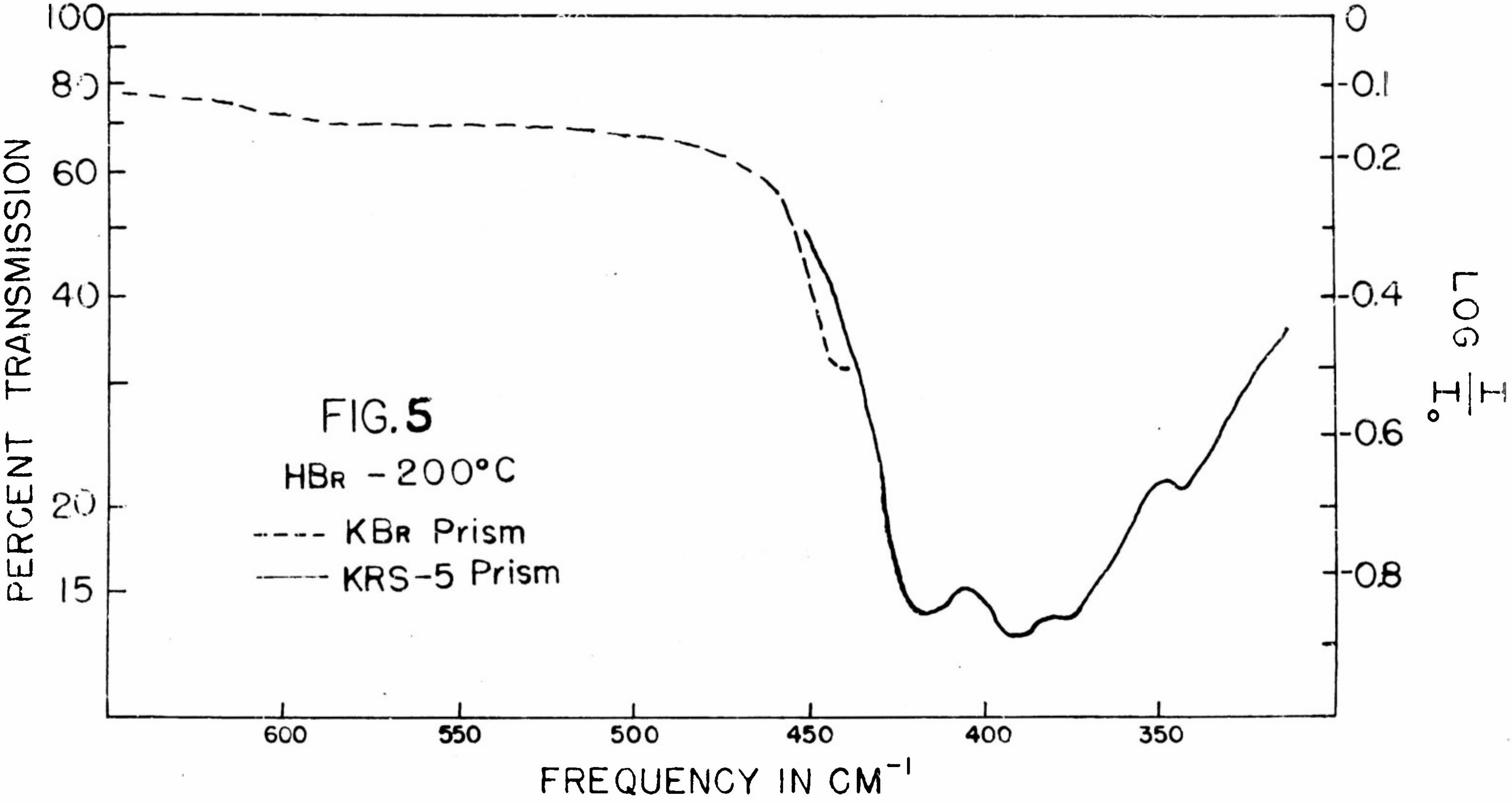

FIG. 5

100
80
60
40
20
15
PERCENT TRANSMISSION
0
-0.1
-0.2
-0.4
-0.6
-0.8
$\text{LOG}\ \frac{I}{I_0}$
600
550
500
450
400
350
FREQUENCY IN CM^{-1}
HBr -200°C
KBr Prism
KRS-5 Prism

of HCl impurity in the HBr. It has been pointed out previously[10] that such a dilute solid solution should show only one sharp line, and the observed line corresponds very closely to the mean of the HCl components, 2729 cm^{-1}. The very weak absorption maxima at about 2660 cm^{-1}, and possibly 2850 cm^{-1}, may actually correspond to the high frequency peaks in HCl. A weak line whose width is ca.100 cm^{-1} has its center at 400 cm^{-1} (Fig. 5) and another very weak absorption is barely evident at 575 cm^{-1}. The structure on the 400 cm^{-1} band is probably caused by water vapor, which has very intense rotational lines in this region.

It was not possible to find a low frequency component of the strong absorption doublet similar to that found in hydrogen chloride. Several of the films showed an absorption region at 2349 cm^{-1}, a frequency identical with that of carbon dioxide, but it was not reproducible.

c. Hydrogen Iodide.

Since hydrogen iodide undergoes a λ-type transition to its low temperature phase at 70°K., nearly the lowest temperature we could reach, an unambiguous spectrum of this phase was not obtained. Instead, a spectrum of a film was taken on KBr at 83°K., (above the transition temperature); the pressure above the liquid nitrogen was then reduced, and the spectrum was followed as the film cooled. The results are shown in Fig. 6. The thin films reached equilibrium after approximately forty minutes while the spectrum of a medium thick film changed slowly through a period of an hour. The spectrum of a very thick film (not reproduced) gave no indication of passing through the transition point although the nitrogen reservoir was maintained at the nitrogen triple point (63°K.) for a period of ninety minutes.

The frequency of maximum absorption, 2120 cm^{-1}, was independent of the temperatu throughout the small range (~15°K.) studied. However, the transition showed itself by the growth of a single sharp spike (width at half-height = approx. 10 cm^{-1}) above

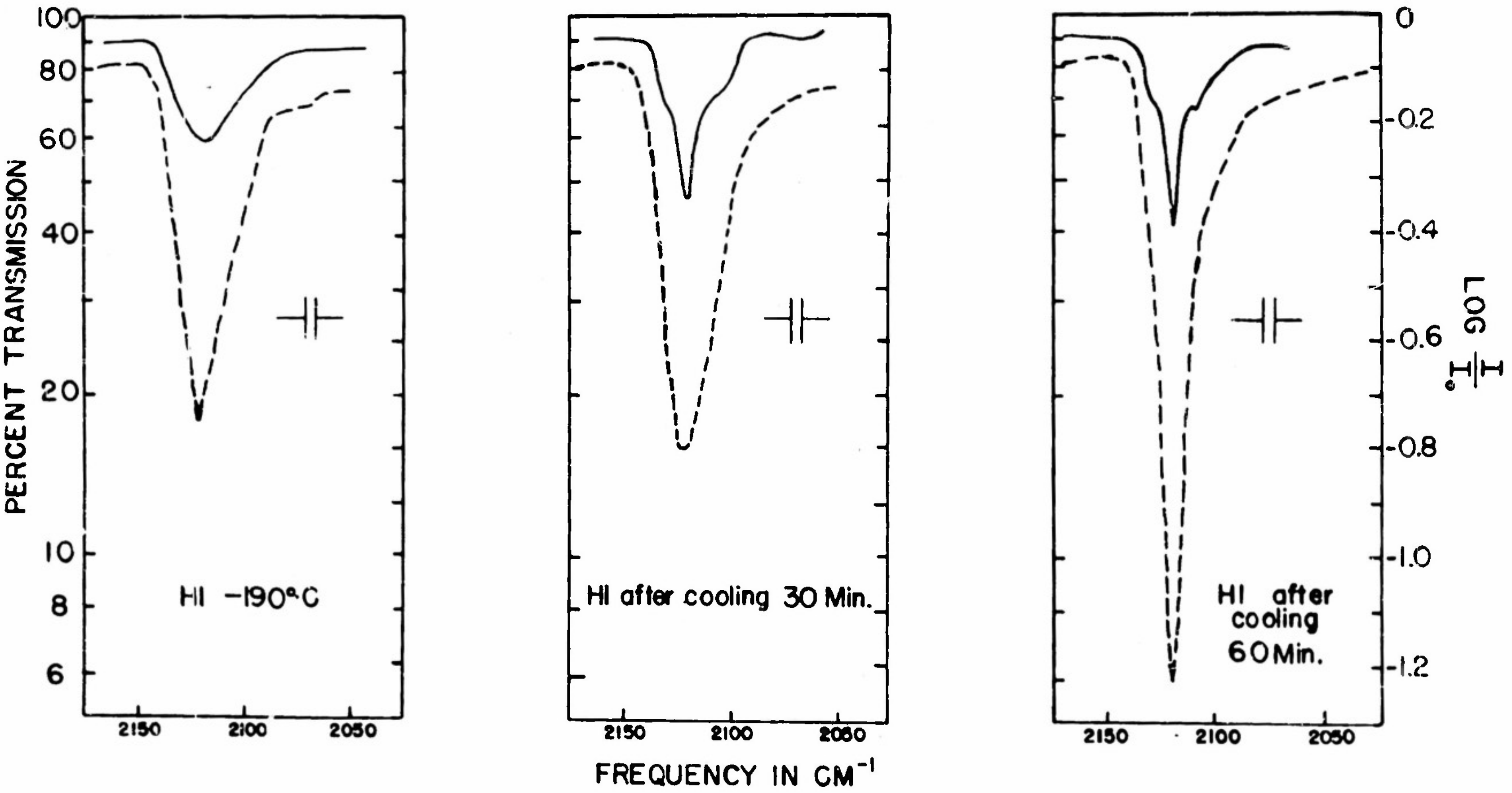
PERCENT TRANSMISSION
100
80
60
40
20
10
8
6
HI −190°C
HI after cooling 30 Min.
HI after cooling 60 Min.
2150
2100
2050
FREQUENCY IN CM^{-1}
LOG $\frac{I}{I_0}$
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2

FIG. 6

the broader peak (width approx. 30 cm^{-1}) characterizing HI above 70°K. It is not clear whether the thin film underwent complete transition or not. The base in B and C of Fig. 6 may be regarded as a remnant of the higher temperature spectrum. However there are indications that in fact there are additional sharp components about 10 cm^{-1} on either side of the central peak, of which one may be just resolved in C.

There also appears to be a weak band at Ca. 2075 cm^{-1} in Fig. 6, and a still weaker band at Ca. 2180 cm^{-1} in the spectrum of a very thick film at 83°K. These appear to be a sum and difference band involving a lattice frequency of about 50 cm^{-}

Crystal Structure of the Hydrogen Halides

According to the available x-ray information, HCl and HBr are both face-centere orthorhombic in their low temperature phase, the lattice dimensions being 5.03, 5.35 and 5.46Å in HCl and 5.56, 5.64 and 6.06Å in HBr.[17] The latter are open to some question because the same investigator found an almost identical orthorhombic structure above 117°K. whereas optical studies[18] indicate an isotropic structure above this temperature and anisotropic structures beneath. HI is reported to have a face-centered tetragonal structure with an axial ratio of 1.08:1[19] (i.e. nearly cubic at all temperatures. However, here too the optical investigation found anisotropy

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[17] G. Natta, Gazz. Chim. Ital. 63, 425 (1933)

[18] A. Kruis and R. Kaischew, Z. Physik Chem. B41, 427 (1938)

[19] B. Ruheman and F. Simon, Z. Physik. Chem. B15, 389 (1931-32)

only beneath 70°K.

If the HCl and HBr structures are face-centered orthorhombic as reported, the x-ray unit cell contains four halogen atoms. The true primitive cell may contain one, two, four or more molecules. On the basis of the present results and the published Raman spectrum, the following conclusions are possible.

(1) The presence of at least two infrared active components in both HCl and HBr demonstrates that there are at least two molecules per primitive unit cell. If there are only two molecules per unit cell they must lie in a plane or in parallel planes because of the orthorhombic symmetry. If there are more than two molecules they still lie in parallel planes unless there is a third infra-red active component. The line at 2616 cm^{-1} is so weak that even if it is a third component the structure is substantially planar.

(2) Unless both of the Raman lines which have been reported in HCl at 2709 ± 5 cm^{-1} and 2759 ± 5 cm^{-1} coincide with the infrared peaks at 2704 and 2746 cm^{-1}, there must be four molecules per unit cell in HCl. It seems probable, therefore, that the unit cell contains four molecules, but it is possible that it contains only two.

(3) If there are but <u>two</u> molecules in a unit cell there are only two basic structural possibilities.

(a) Both of the molecules lie in a single plane and the crystal is built of planes containing parallel zig-zag chains such as that illustrated in Fig. 7.

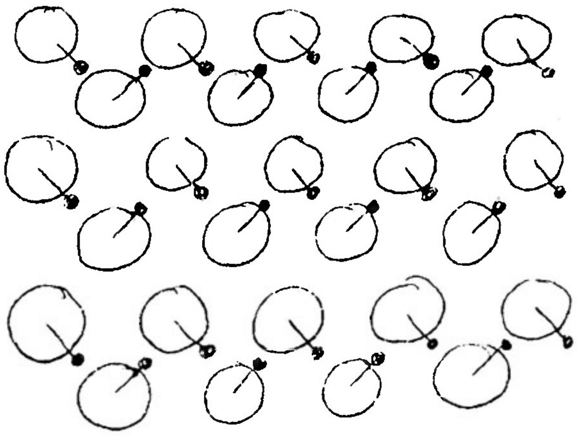

Fig. 7

In this structure each sheet can be obtained from the others by simple translation.

(b) All of the molecules in a plane are parallel but the two molecules lie in alternate planes. This possibility is illustrated in Fig. 8 and would consist alternately of planes a and b.

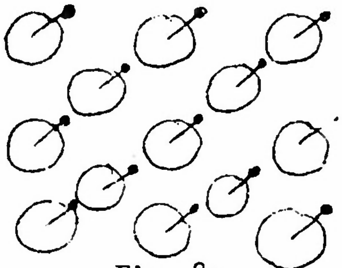

Fig. 8a

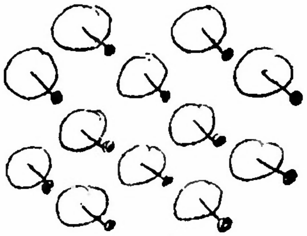

Fig. 8b

This second possibility is ruled out by the studies of dilute solutions of HCl in DCl crystals[10] which show that there is an angle of 102° between interacting pairs of molecules and that there is only one kind of pair showing appreciable interaction. It is unreasonable to anticipate that the interacting pair is not the hydrogen bonded pair.

(4) If there are <u>four</u> molecules per unit cell the number of reasonable possibilities is still limited.

(a) If the four molecules lie in a single plane and it is assumed (a) that one hydrogen atom is bonded to each chlorine and (b) that the angle between all hydrogen bonded pairs is identical, the crystal must consist of the planes shown in Fig. 9 and successive planes must be derived from each other by simple lattice translation.

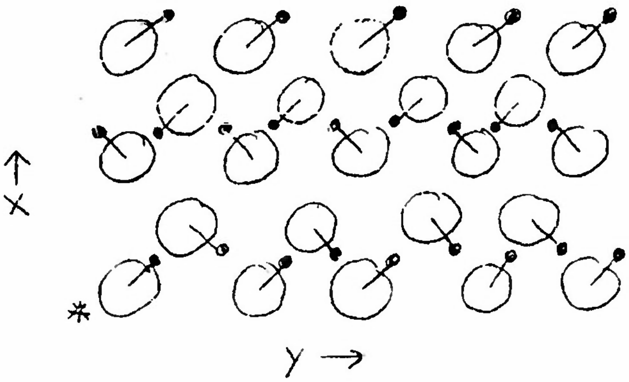

Fig. 9

Since the plane above or beneath can be derived by either of two lattice translations from the starred molecule to the face-centered position in the xz or yz plane, two structures of this type are possible.

(b) If two molecules each lie in two parallel planes, the structure must be built from planes like that in Fig. 7, but the directions of the chains in adjacen planes must be reversed. There are two possibilities of this sort, depending on whether the reversed plane is displaced by a half unit cell in the x or y direction.

(c) If one molecule lies in each of four planes, the structure is similar to Fig. 8, planes c and d being obtained by reversing the direction of the chains in a and b. This structure is ruled out by the same arguments as is that of par. 3b.

It seems most likely then that the structure of HCl (and probably also of HBr) is that of par. 4a or 4b. In either case the crystal is built of zig-zag chains, in one case anti-parallel in a single plane, in the other anti-parallel in adjacent planes.

Not as much can be said about the structure of HI. A single sharp component of the stretching vibration would be consistent with the tetragonal x-ray structure. In this case two basic structural possibilities are possible: (a) the molecules are arranged in parallel or anti-parallel chains along the tetragonal axis or (b) sets of four are arrayed perpendicular to the tetragonal axis. However, as pointed out before it is exactly this point which remains uncertain in the spectrum.

The structure is almost certainly different from HCl and HBr, for the observed peak is probably too sharp to be interpreted as an unresolved pair of peaks; only by this interpretation could a similar structure be supported. A final conclusion in this case must await further study.

The Angle Between Molecules in HCl and HBr

In an orthorhombic crystal the dipole moment generated by each normal vibration must be along the x, z or z axis, or in the present planar case along the x or y axis Since the infrared intensity is proportional to $(\mu_x)_{01}^2$ or $(\mu_y)_{01}^2$, then if moments are developed along the bond directions and additivity of moments is assumed, the intensity of each component is proportional to the square of the direction cosines of the molecular axis. It therefore follows immediately that the intensity ratio of the two components is given by the expression

$$\frac{I_x}{I_y} = \tan^2 \alpha /2 \qquad (1)$$

where α is the angle between bonds.

An estimate of the relative integrated intensities was made by comparing the product of the peak intensities and the line width at half of the maximum absorption coefficients. The ratios obtained for four HCl films whose peak absorption occurred in a suitable range was 2.25 (Fig. 2), 1.62, 1.69 and 1.83. The corresponding values of α (or $\pi - \alpha$) were 113°, 104°, 105° and 107°. The reason for the variation is not known although it may be that the films were partially oriented. In this connection it should be noted that the ratio of peak intensities was only 1.17 on the single film deposited on NaCl whereas values 1.30, 1.32 and 1.69 were obtained for those deposited on KBr.

Similar variations were found by the previous investigators,[2,3] but in all cases the line at 2704 cm^{-1} was more intense, although films were deposited on both salt plates and metal mirrors.

If in fact the films were partially oriented, the significance of these angles is open to question. Even if there is no orientation effect the angles may be in error because of a failure of the initial assumptions. It should be noted that this same objection applies to the angles previously measured by Hiebert.[10]

When the same estimate was made for HBr, ratios of 1.28, 1.26, and 1.23 were obtained from three films, all of them on KBr. The corresponding mean angle is either 97° or 83°. Although the same objections apply here as in the case of HCl, it does seem very likely that the intermolecular angle actually is much nearer to 90°. This result is in accord with the x-ray structures.

Force Constants in the HCl and HBr Crystals

If it is assumed that the coupling between internal and external motions of the molecules is negligible, and it is shown in appendix A that this true to a good approximation, the potential energy change when the molecules in a crystal are distorted is

$$2V = \sum_{i=1} \sum_{j=1} \sum_{k=1}^{N} \sum_{\ell=1}^{N} f_{ij}^{kl} r_i^{k} r_j^{\ell} \tag{2}$$

where r_i^k and r_j^ℓ are the i-th and j-th internal displacement coordinates of the k-th and ℓ-th unit cells.

If the momentum conjugate to an r is designated p, the kinetic energy is

$$2T = \sum_i \sum_j \sum_k \sum_\ell g_{ij}^{k\ell} p_i^k p_j^\ell \tag{3}$$

It is worth noting here that the kinetic energy contains cross terms only between coordinates both of which are common to the same molecule.

In the case of motions which may give rise to spectral activity, either infrared or Raman, corresponding coordinates of all unit cells are equal. That is,

$$r_i^1 = r_i^2 = \ldots\ldots\ldots\ldots\ldots r_i^k = r_i \tag{4}$$

$$p_i^1 = p_i^2 = \ldots\ldots\ldots\ldots\ldots\ldots p_i^k = p_i \qquad (5)$$

so that eqns. (2) and (3) become

$$2V = N \sum_i \sum_j f_{ij} r_i r_j \qquad (6)$$

$$2T = N \sum_i \sum_j g_{ij} p_i p_j \qquad (7)$$

where

$$f_{ij} = \sum_{k=1}^{N} f_{ij}^{k\ell} \qquad (8)$$

$$g_{ij} = \sum_{k=1} g_{ij}^{k\ell} \qquad (9)$$

The factor N, the total number of unit cells in the crystal, factors from the equations of motion so that the secular determinant is simply

$$\left| gf - \lambda I \right| = 0. \qquad (10)$$

Its dimensions equal the number of internal coordinates in a single unit cell. In the problem at hand these are just the four H-Cl stretching coordinates.

If the HCl and HBr crystals are orthorhombic, they must belong to one of the D_{2h}, D_2, or C_{2v} space groups. No matter which one, an appropriate set of symmetry coordinates for a unit cell containing four molecules is

$$S_1 = 1/2 \; (r_1 + r_2 + r_3 + r_4)$$
$$S_2 = 1/2 \; (r_1 + r_2 - r_3 - r_4)$$
$$S_3 = 1/2 \; (r_1 - r_2 - r_3 + r_4)$$
$$S_4 = 1/2 \; (r_1 - r_2 + r_3 - r_4) \qquad (11)$$

The symmetry classification of the coordinates depends on the particular structure. These coordinates factor the secular determinant and yield

$$\lambda_i = G_{ii}F_{ii} \qquad , \qquad i = 1, \ldots\ldots 4. \tag{12}$$

In this equation

$$G_{ii} = \mu_H + \mu_{Cl} \tag{13}$$

if μ_H and μ_{Cl} are the reciprocals of the masses of H and Cl respectively. It is clear from equation (12) that for an orthorhombic crystal with four molecules per unit cell there are but four independent force constants. In terms of the symmetry force constants determined from eq. (12) they are

$$\begin{aligned} f_{11} = f_{22} = f_{33} = f_{44} &= 1/4\ (F_{11} + F_{12} + F_{13} + F_{14}) \\ f_{12} &= 1/4\ (F_{11} + F_{22} - F_{33} - F_{44}) \\ f_{13} &= 1/4\ (F_{11} - F_{22} - F_{33} + F_{44}) \\ f_{14} &= 1/4\ (F_{11} - F_{22} + F_{33} - F_{44}) \end{aligned} \tag{14}$$

Assuming that HCl and HBr are actually built of anti-parallel zig-zag chains, we shall designate the hydrogen bonded pair in the first chain by r_1 and r_2, the anti-parallel pair by r_3 and r_4. Then λ_2 and λ_3 are infrared active, with λ_2 polarized along the chain axis and λ_3 perpendicular to it. Although all four may be Raman active, we will assume that the observed Raman lines in HCl are λ_1 and λ_4. The most reasonable assignments of the observed frequencies in HCl are then as follows.

	A	B
ν_1	2709	2759
ν_2	2704	2746
ν_3	2746	2704
ν_4	2759	2709

Other permutations are possible but these two assignments are the only ones consistent with the assumption that no other interactions are nearly as strong as those between hydrogen bonded pairs. This assumption is justified by the previous finding that only one variety of significantly interacting molecular pair occurs in dilute solutions of HCl in DCl. We thus obtain the force constants

$$f_{11} = 4.31 \times 10^5 \text{ dynes/cm.} \qquad (\text{gas} = 4.806 \times 10^5 \text{ dynes/}$$

$$f_{12} = f_{34} = \mp .072 \times 10^5$$

$$f_{13} = f_{24} = .012 \times 10^5$$

$$f_{14} = f_{23} = \pm .006 \times 10^5$$

It is of some interest to compare the principal force constant f_{11} and the force constant connecting hydrogen bonded molecules f_{12}, with those obtained from the data of Hiebert and Hornig on molecular pairs. In the case of a pair of HCl molecules which are coupled to each other

$$4\pi^2 \nu_1^2 = (f_{11} + f'_{12})\,(\mu_H + \mu_{Cl})$$

$$4\pi^2 \nu_2^2 = (f_{11} - f'_{12})\,(\mu_H + \mu_{Cl})$$

It is to be anticipated that $f'_{12} \leqq f_{12}/2$ since according to eq. (9) f_{12} is the sum of the interactions between a single molecule (1) and all molecules (2). If only the two nearest neighbor molecules in the chain contributed, the factor would be exactly 1/2. Using 2715 cm^{-1} and 2737 cm^{-1} for the frequencies, one obtains

$$f_{11} = 4.29 \times 10^5 \text{ dynes/cm.}$$

$$f_{12}' = \pm .035 \times 10^5 \text{ dynes/cm.,}$$

both in good agreement with those derived from the present work.

The only alternative interpretation of the spectrum, that the Raman line at 2709 cm^{-1} actually coincides with the infrared line at 2704 cm^{-1}, and that the fourth component is the infrared line at 2616 cm^{-1}, leads to a somewhat different result, namely, that $f_{11} = 4.20 \times 10^5$ dynes/cm. and the three cross-terms equal ± 0.14, ± 0.078 and $\pm 0.058 \times 10^5$ dynes/cm. The principal force constant is in substantial agreement but the existence of three sizeable coupling constants leads to the prediction that three different kinds of interacting pairs would be observed in Hiebert's experiment. These three pairs would have had vibration frequencies separated by 12 cm^{-1}, 14 cm^{-1} and 24 cm^{-1} from the central peak. The first two coincide well with the 12 cm^{-1} separation observed, but the absence of the last peak rules this interpretation out.

Since the Raman spectrum of low temperature HBr is unavailable, a complete treatment is impossible. However, if it is assumed that coupling between chains is negligible, and it is almost certainly less important than in HCl, the result is

$$f_{11} = 3.45 \times 10^5$$

$$f_{12} = .048 \times 10^5 \qquad (\text{gas} = 3.85 \times 10^5 \text{ dynes/cm.})$$

In HI it is only possible to obtain a rough value of the principal force constant for comparison with the gas value. It is

$$f_{11} = 2.66 \times 10^5 \qquad (\text{gas} = 2.95 \times 10^5 \text{ dynes/cm.})$$

It is seen then that there is evidence of considerable intermolecular interaction, whether or not it be called hydrogen bonding, in all three molecules. Even in HI the fundamental frequency decreases 100 cm^{-1} and the principal force constant by 9.5% from the gas value.

Aside from the stretching modes the molecules may also oscillate about axes through their centers of gravity. Since each molecule of the unit cell has two of these motions, eight different modes of this type may be expected; six of them may be infrared active. They have not all been observed. Their magnitude may be estimated as approximately 266 cm^{-1} in HCl from the combination band at 2991 cm^{-1}. If coupling is neglected

$$4\pi^2 \nu_T^2 = k_T r_0^2/I$$

where r_0 is the equilibrium internuclear distance, I the moment of inertia and k_T the force constant for perpendicular displacements of the protons. Using 266 cm^{-1}, we find roughly that

$$k_T = 0.041 \times 10^5 \text{ dynes/cm.}$$

It is interesting that this is of the same order of magnitude as the intermolecular interaction constants found previously. If the corresponding torsional frequency in HBr is 240 cm^{-1}, obtained from the band at 2660 cm^{-1}, the force constant is

$$k_T = 0.033 \times 10^5 \text{ dynes/cm.}$$

Conclusion

The low temperature phases of both HCl and HBr are built from antiparallel zig-zag chains of hydrogen bonded molecules with angles not too different from 90° between adjacent molecules. This structure is qualitatively similar to that found in gaseous HF and indicates that the structure is based, not on a dipole array, but on hydrogen bonds to the non-bonding orbitals of the adjacent molecule. This has the effect of preserving external valence angles. If the angle between molecules is actually as great as 107°, as the measurements on HCl indicate, there may be a fair amount of hybridization in HCl.

Appendix A

In the calculation of the force constants in the HCl and HBr crystals, it was assumed that to a good approximation there was no interaction between internal and external motions of the molecules in a crystal. This can be shown as follows. If we define the symmetric matrix $H = \frac{FG + GF}{2}$, then according to second order perturbation theory the ith eigenvalue of a set of coupled harmonic oscillators is displaced by an amount

$$\Delta\lambda_i = \sum_{j \neq i} \frac{|H'_{ij}|^2}{\lambda^0_i - \lambda^0_j} \qquad (1)$$

by the introduction of the coupling H'_{ij}. In eq. (1) $\lambda^0_i = 4\pi^2 \nu^{0\,2}_i c^2$, if ν^0_i is the frequency (cm^{-1}) in the absence of the coupling elements. In the present case the eigenvalues, λ^0_j, corresponding to lattice frequencies may be neglected with respect to those representing the internal vibrations. Eq. (1) can then be put into the form

$$32\pi^4 c^4 \nu^{0\,3}_i \Delta\nu_i = \sum_{j \neq i} |H'_{ij}|^2 \qquad (2)$$

If it is assumed that the order of magnitude of the coupling elements F'_{ij} is the same as those coupling internal vibrations, or the diagonal elements for the torsional lattice vibrations, then the frequency shift arising from coupling between internal and lattice modes would be approximately 0.2 cm^{-1}. Even if this estimate were in considerable error it would still be justifiable to neglect the coupling to lattice modes when solving the problem of the internal vibrations.

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Infrared Spectra and Structure of Crystalline Ammonia Hydrates

By R. D. Waldron and D. F. Hornig

Received August 20, 1953

Recent very careful studies of the heat capacity and thermodynamic properties of $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$,[1] as well as earlier studies of the solid phases of the ammonia–water system,[2] have demonstrated that the two ammonia hydrates are well-defined compounds of exact composition.

The structure of these compounds is of some interest since they might exist either as simple hydrates or as ionic crystals. Although considerable experimental evidence exists to indicate that aqueous solutions of ammonia are only slightly ionized,[3] Hildenbrand and Giauque regard the crystalline hydrates as ammonium salts, *i.e.*, $(NH_4)OH$ and $(NH_4)_2O$.

No previous spectroscopic studies of the solid phases of the NH_3–H_2O system were uncovered in a survey of the literature although the infrared and Raman spectra of aqueous ammonia[4,5] have been obtained.

In the present study mixtures of NH_3 and H_2O vapor were admitted to a low temperature infrared cell[6] and condensed on NaCl or KBr plates cooled with liquid nitrogen. The spectra obtained were consistent with an ammonia hydrate structure and definitely exclude an ionic structure.

Results

Figure 1 shows the spectra obtained for mixtures of NH_3 and H_2O at −195°, together with those of pure NH_3, H_2O and NH_4X for comparison. It is immediately clear that the spectra bear little resemblance to that of the NH_4^+ ion, and the absence of the NH_4^+ ion bending vibration at about 1400 cm.$^{-1}$ is conclusive. On the other hand, they closely parallel the spectra of crystalline NH_3 and H_2O, although there are some clear differences.

The interpretation of the low frequency region of the spectrum is most obvious. The strong ice band at 812 cm.$^{-1}$[7] appears in the spectrum with excess H_2O (A) but not in (B) or (C), so that the H_2O in the compounds is included in a lattice different from ice. If the 812 cm.$^{-1}$ band is a lattice vibration connected with the torsional oscillations of the H_2O molecules, the H_2O molecules cannot be as tightly bound in the hydrates as in ice; *i.e.*, one of the O–H · · · O bonds must have been replaced by an O–H · · · N bond. The symmetrical bending vibration of ammonia, which occurs at 1060 cm.$^{-1}$ in the pure crystal,[8] appears at 1102 cm.$^{-1}$ in $NH_3 \cdot H_2O$ (B) and as a doublet, 1020 and 1091 cm.$^{-1}$, in $2NH_3 \cdot H_2O$ (C). The doubling probably indicates that the environment of the two NH_3 molecules is not identical. Excess NH_3 (D) produces an additional shoulder at 1069 cm.$^{-1}$ which may be identified as free NH_3.

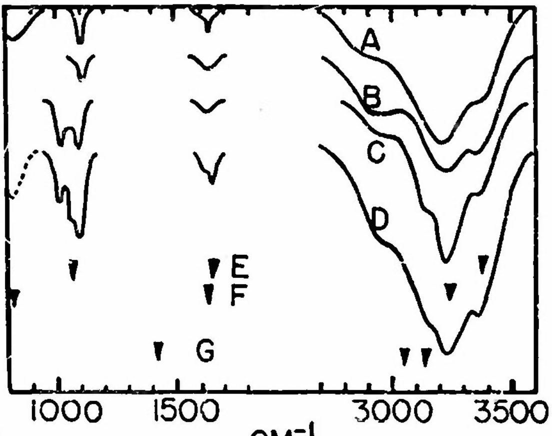

Fig. 1.—Infrared spectra of crystals of the NH_3–H_2O system at −195° together with comparison spectra: A, $NH_3 \cdot H_2O + H_2O$; B, $NH_3 \cdot H_2O$; C, $2NH_3 \cdot H_2O$; D, $NH_3 + 2NH_3 \cdot H_2O$ (some frost formation entailed by a small vacuum leak); E, crystalline NH_3; F, Ice; G, ammonium ion.

Both the bending vibration of H_2O and the doubly degenerate bending vibration of NH_3 may contribute to the absorption near 1625 cm.$^{-1}$. However, since the symmetric bending vibration is far more intense than the degenerate one in both gaseous and crystalline NH_3, it does not seem likely that very much of the observed absorption in this region is caused by NH_3.

The stretching region cannot be analyzed so straightforwardly. The peak at 2950 cm.$^{-1}$ occurs in the spectrum of both hydrates but is relatively more intense in that of $NH_3 \cdot H_2O$ (B). It is probably too low in frequency to be ascribed to OH, since only acidic OH in very strong H-bonds absorbs at so low a frequency, and then only rarely. Similarly, NH · · · N bonds would probably not lead to such a low frequency, leaving an NH · · · O bond as the most likely explanation for this band. If this is correct, it seems likely that in $2NH_3 \cdot H_2O$ only one of the ammonia molecules is involved. The peak at 3140 cm.$^{-1}$ (C) belongs to $2NH_3 \cdot H_2O$ and may represent a weaker NH · · · O bond from the second NH_3 molecule.

The remaining peaks at 3220 and 3365 cm.$^{-1}$ are characteristic of hydrogen bonded O–H and N–H vibrations and cannot be assigned in detail. Although some of the 3220 cm.$^{-1}$ absorption in A is

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undoubtedly caused by ice and some of the 3365 cm.$^{-1}$ absorption in D by ammonia, it should be noted that the addition of NH_3 in passing from B to C increases the relative intensity of the 3220 cm.$^{-1}$ peak. It follows therefore that NH_3 also absorbs in this region.

Structural Conclusions

It seems clear that neither hydrate of ammonia contains ammonium ions. In addition to the reasons previously outlined, the presence of NH_4^+ ion would imply OH^- or O^{--} ions. In the former case a frequency higher than any observed would be expected (OH^- absorption occurs at 3638 cm.$^{-1}$ in NaOH[9]); in the latter there is no explanation for the two highest frequencies.

$NH_3 \cdot H_2O$ is a bimolecular crystal. There are five H atoms and only three unshared electron pairs per mole, so at least two H atoms must be either nonbonded or very weakly bonded. If, as in crystalline NH_3, three weak hydrogen bonds are formed to the single electron pair of NH_3, only two strong bonds can be formed. From the spectrum it can be concluded that a strong NH · · · O bond is formed (2.8 Å. or less from the magnitude of the frequency shift observed) and that both hydrogens from H_2O are involved in at least weak hydrogen bonds (since free H_2O absorbs near 3700 cm.$^{-1}$). This implies at least one O–H · · · N bond.

$2NH_3 \cdot H_2O$ is a trimolecular crystal. The two NH_3 molecules appear to be non-equivalent. The structure includes at least one strong NH · · · O bond and all of the hydrogens from H_2O are hydrogen bonded.

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