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Vibrational Spectrum of Crystalline HF and DF*

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Infrared spectra of pure crystalline HF and DF have been obtained over the region 30-4000 cm⁻¹, and the spectra of the dilute isotopic mixed crystals have been studied in the intramolecular region 2000-4000 cm⁻¹. Unlike previous workers, we find four bands in the stretching region of pure DF crystals, as well as the previously-reported four in the corresponding region of the HF spectrum. Direct observation of a lattice band near 200 cm⁻¹ in both HF and DF, together with the line spacing in the stretching region permits an unambiguous assignment of the extra pair of lines in the intramolecular region as combination bands. The Raman spectra of crystalline HF and DF reveal four lines in the stretching region and one lattice transition. With the aid of simple intensity rules and correlations with the other hydrogen halides, a complete assignment of the vibrational bands is made except for the librational region, where the multiplicity of lines and the peculiar behavior of one of them under different deposition conditions make a firm interpretation impossible. The assignment is discussed with reference to results obtained by inelastic neutron scattering. Within experimental error each Raman line is coincident with an infrared line, and the structural implications of this fact are discussed.

INTRODUCTION

SINGLE-crystal x-ray diffraction study of HF¹ re-A ported that the crystal is built from infinite zigzag hydrogen-bonded chains. This x-ray study could not distinguish between the space group D_{2h}^{17} -Bmmb, in which the sense of the chains is random along the Y axis of the crystal, and the ordered structure D_{2h}^{16} -Pmnb with four molecules per primitive cell, in which each zigzag chain has four antiparallel nearest neighbors related by centers of inversion. This structure is shown in Fig. 1, together with the structure obtained when all chains are parallel, C_{2v}^{12} . An infinite planar zigzag chain of heteronuclear diatomic molecules has two stretching frequencies in either infrared or Raman; the infrared and Raman spectra coincide if the threedimensional structure is D_{2h}^{17} , but the mutual exclusion rule is operative if the structure is D_{2h}^{16} . Three previous investigations of the infrared spectrum of crystalline hydrogen fluoride,²⁻⁴ however, have established that four components appear in the intramolecular region of the HF spectrum. Giguère and Zengin³ originally suggested that two of the lines, somewhat weaker than the other two, were in fact a pair of Raman-active components appearing in infrared because of a breakdown of selection rules brought about by crystalline disorder. These authors assumed the structure D_{2h}^{17} . Sastri and Hornig⁴ were able to show, on group theoretical grounds, that this reasoning was incorrect, since for the disordered crystal the infrared and Raman

spectra are expected to coincide. Their spectra of dilute mixtures of HF in DF and vice versa suggested that. as expected, the forces between molecules in different chains are much weaker than the forces between hydrogen-bonded molecules. The spectrum of dilute isotopic mixtures of HF and DF showed only one pair of lines originating from pairs of solute molecules isolated in the isotopic solvent lattice. The members of



this pair are hydrogen bonded to each other, and no evidence for non-hydrogen-bonded pairs was found. These facts established that interchain forces are much weaker than intrachain forces; they could not, however, establish whether the interchain coupling force constant was zero, or simply very small. In short, the structural question could not be answered from infrared studies of mixtures of HF and DF.

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¹ M. Atoji and W. N. Lipscomb, Acta Cryst. 7, 173 (1954).

² G. L. Hiebert (unpublished results).

P. A. Giguère and N. Zengin, Can. J. Chem. 36, 1013 (1958).
 M. L. N. Sastri and D. F. Hornig, J. Chem. Phys. 39, 3497

^{(1963).}



FIG. 2. Low-temperature Raman apparatus.

The published spectra of the lattice region of crystalline films of HF are not in good agreement. In particular Sastri and Hornig⁴ found a well-defined band near 790 cm⁻¹ in HF, while Giguère and Zengin³ found only a broad, featureless shoulder in that region. Sastri and Hornig reported a total of four lines which seemed librational in nature, while only three are predicted from a group-theoretical analysis for either D_{2h}^{16} or D_{2h} ¹⁷. Finally, the spectrum of the region below 350 cm⁻¹, where the pseudotranslational frequencies lie, had not been observed.

It seemed important to reinvestigate and extend the studies on pure HF and DF throughout the infrared region in order to clarify the assignment of the observed bands. It seemed possible to elucidate the structure of HF by also obtaining Raman spectra, which had never been observed in HF or DF. Not only are the infrared and Raman spectra predicted to be noncoincident for the structure D_{2h} ¹⁶, but six Raman-active pseudotranslations are predicted for this structure, where only three are anticipated for the structure D_{2h}^{17} .

I. EXPERIMENTAL

The HF used in this work was obtained from the Matheson Company and had a stated purity of 99.9%. Noncondensible gases were removed by cooling the lecture bottle to -195° C and pumping. The middle third of the contents of the lecture bottle was then distilled from 0°C to a monel storage cylinder at - 195°C in a copper vacuum system. This distillate was used without further purification.

KDF₂ was decomposed by strong heating to prepare DF. The KDF₂ was synthesized from KHF₂ (Harshaw, 99%) and D₂O (Matheson, Coleman and Bell, 99.5%) by repeated recrystallization. The KDF₂, contained in a copper retort, was heated in a controlled manner to dry it: only at temperatures above 225°C and only after 5 h of heating and pumping was DF condensed into a monel storage cylinder. DF was subsequently distilled from the cylinder as needed. The relative amounts of HF and DF in the sample were estimated from the infrared intensities of the HF and DF portions of the spectrum of a crystalline film of the material. To do this it must be noted that $(I_i/\nu_i) = \text{constant}$,

where I is the integrated intensity of the band, ν is the frequency, and i is the isotopic species.⁵ Using crystal frequencies, it was found that $I_{\rm HF} \simeq 1.85 I_{\rm DF}$, and the product DF was found to be 99% isotopically pure. In obtaining infrared spectra a standard low-temperature cell of copper and stainless steel⁴ was used. For cell windows and backing plates various combinations of AgCl, CsI, silicon, polyethylene were used. Only CsI was attacked by HF, and only if the temperature of the substrate rose above -100 °C. A copper-constantan thermocouple squeezed against the backing plate recorded its temperature, which was $-185^{\circ}\pm 2^{\circ}$ C during experiments. Deposition at temperatures higher than -185°C was achieved by inserting a Teflon plug into the bottom of the coolant reservoir before adding coolant. This sufficiently reduced the rate of cooling $(\sim 10^{\circ}/\text{min})$ so that a sample could be sprayed on at any desired temperature below -110° C.

Raman spectra of polycrystalline HF and DF were obtained with the apparatus shown in Fig. 2. The flat-ended, unsilvered Dewar was Pyrex, but the sample tube was made of fused quartz, a material which is known to be resistant to HF attack.⁶ The procedure was to cool the sample tube with a fast stream of



FIG. 3. Infrared spectra of thin films of HF and DF stretching regions.

⁵ B. L. Crawford, Jr., J. Chem. Phys. 20, 977 (1952).

⁶ J. G. Ryss, *Chemistry of Fluorine and Its Inorganic Compounds*, translated by Firma Haimson (U.S. Atomic Energy Commis-sion Technical Information Service Extension, Oak Ridge, Tenn., 1960), Vol. 1.

nitrogen gas which had been passed through a double copper coil immersed in liquid nitrogen. If a sufficient pressure drop occurs near the sample tube, some of the nitrogen condenses, and temperatures close to -195° C were achieved in this way. The spectra shown below were recorded at $-193^{\circ}\pm 2^{\circ}$ C. A 5-ml sample, the typical volume, was distilled into the tube at temperatures below -100° C, and was frozen in a few minutes. If, at the conclusion of an experiment, the sample was distilled out of the tube quickly, only trace etching occurred. In this way it was possible to use one of the tubes three times. The total absence of the 790-cm⁻¹ breathing mode of SiF₄ from the spectra indicates negligible etching.

The infrared spectrometer used in the region 200– 4000 cm⁻¹ was a Beckman IR-12. The instrument was calibrated with the standard gases at low pressures (CH₄, NH₃, HCl, H₂O) using the known line positions.^{7,8} The spectral slitwidth was 1–2 cm⁻¹ in the 3000-cm⁻¹ region, and rose to 4 cm⁻¹ near 200 cm⁻¹. Calibration is accurate to ± 0.2 cm⁻¹ but observed frequencies are accurate to only ± 2 cm⁻¹ for sharp peaks and ± 3 cm⁻¹ for broad bands because of the great bandwidths.

The Raman spectra reported here were obtained on a Cary Model 81 photoelectric spectrometer. The source was a Toronto arc, and the 4358-Å exciting line was isolated by the filter solution supplied with the instrument. This removed all unwanted mercury lines except the 4916-Å line, which is discussed below. Spectral slitwidths were 10 cm⁻¹ for all reported spectra.

The Cary 81 was calibrated by removing the filter solution and recording the positions of the mercury lines. Additional calibration points were obtained by observing the spectrum of liquid benzene under high resolution. Reported HF and DF frequencies are accurate to $\pm 3-4$ cm⁻¹.

In the far infrared, spectra were obtained by interferometric techniques using an RIIC "Fourier Spectrophotometer," Model 520. Mylar beam splitters of



FIG. 4 Infrared spectrum of a thick film of DF in the stretching region.

 TABLE I. Frequency separations of infrared lines in stretching region of HF and DF.

	100% HF	99% DF		
ν	Δν	ν	Δν	
3585 cm ¹] 101	2712		
3404		2526)	
3275	339	2495	234	
3065		2292)3	
1% HF		1% DF		
3490 3345 3277 3190	213	$ \begin{array}{c} 2605 \\ 2470 \\ 2404 \\ 2353 \end{array} $ 20)1	

0.0005 and 0.00025 in. were used together with a highpressure mercury lamp source and a Golay detector. The instrument was evacuated to pressures below 50 μ to remove water-vapor absorptions. The Golay output was digitized and recorded on computer cards at preset intervals in mirror travel, every 8 μ in these experiments. Spectra were obtained by Fourier transformation of the digitized interferograms, this computation being done on an IBM 7094 computer. The spectra shown below were ratioed by the computer: an averaged background spectrum was subtracted from an averaged sample run. The spectra shown were obtained from interferograms of 320 points, so that the resolution is just under 4 cm⁻¹. During each run, at least one interferogram of 2-cm⁻¹ resolution was made to check for fine structure. Calibration of the FS-520 was achieved by observing the spectrum of water vapor and is accurate to ± 1 cm⁻¹. Again the chief uncertainty lies in determining the frequencies of maximum absorption, which are accurate to ± 3 cm⁻¹.

II. RESULTS

The infrared spectra in the stretching region of crystalline films of pure HF and DF are shown in Fig. 3. If the films are prepared by depositing a burst of vapor at high (~ 1 atm) pressure onto the substrate at temperatures near -125°C, when the substrate is cooled to -185°C the linewidths are only 70% of the widths observed in films deposited directly at -185°C. The spectra reported here, unless otherwise indicated, are of films prepared in the former manner.

Figure 3 shows spectra essentially identical to those reported previously,^{3,4} four lines appearing in the HF spectrum but only two in that of DF. Study of a thicker film of DF, however, reveals a shoulder near 2495 cm⁻¹ and a weak line at 2712 cm⁻¹ (Fig. 4). If each fundamental stretching vibration has a different symmetry species, then the ratio of any HF frequency to its DF counterpart ought to be constant and nearly equal to $(\mu_{DF}/\mu_{HF})^{1/2}$, or the root of the reduced mass

⁷ Tables of Wavenumbers for the Calibration of Infrared Spectrometers (Butterworths Scientific Publications, Ltd., London, 1961). ⁸ K N Rao R V de Vore, and E K. Plyler, L Res Natl.

⁸ K. N. Rao, R. V. de Vore, and E. K. Plyler, J. Res. Natl. Bur. Std. (U.S.) 67A, 351 (1963).



FIG. 5. Raman spectra of HF and DF in stretching region.

ratio, 1.38. That is, the ratios of splittings should equal the same constant value when each line is a fundamental. Table I shows that the separation between the two strongest lines collapses to nearly the predicted value in going from HF to DF. On the other hand, the separation between either strong line and the weaker line to the high-frequency side remains constant in going from HF to DF.

The Raman spectra of HF and DF in the molecular stretching region are shown in Fig. 5. Background scattering around the 4916-Å mercury line (2602-cm⁻¹ Raman shift) complicates the high-frequency portion of the DF spectrum. We have compensated for this by subtracting the appropriately scaled background scat-



FIG. 6. Infrared spectra of dilute solid solutions of HF and DF. Stretching region of the solute is shown.

tering from HF in the same region; this leaves the dashed line shown. In number of lines, line spacing, intensity, and frequency, these spectra are strikingly similar to the infrared spectra of the pure crystals. No attempt was made to locate the analogs of the two weak peaks in infrared spectrum of DF. The data here are summarized in Table II.

Infrared spectra of 1%-2% solid solutions of HF in DF, and vice versa were also studied. These are shown in Fig. 6. Isolated molecules of the isotopic guests have their fundamental vibration at 3277 cm^{-1} (HF) and 2404 cm^{-1} (DF). The breadth of these lines is 20 cm^{-1} at half height for HF and 19 cm⁻¹ for DF, somewhat sharper than the values of 55 and 40 cm⁻¹ reported previously.⁴ Much weaker shoulders, one on each side of the singlet line, have been assigned as the spectrum of pairs of isotopic guests.⁴ One additional line occurs in both dilute solutions: at 3490 cm^{-1} in dilute HF and at 2605 cm^{-1} in dilute DF. These lines have been observed previously,⁴ but not explained. If the con-

	HF			DF				
	Depositio -125°	n at C	Deposition —185°(n at C	Depositio -125°	on at C	Depositio 	on at C
	ν	$\beta_{1/2^{\mathbf{B}}}$	v	$\beta_{1/2}$	v	$\beta_{1/2}$	ν	$\beta_{1/2}$
Infrared ^b	3585 cm ⁻¹		3590		2712		2710	
	3404 3275	50	3406 3275	75	2526 2495	27	2530 2495	39
	3065	100	3067	130	2292	52	2294	75
	1133-1200	144	1150-1200	88	855-900	100	855-905	95
	962-1025	104	975-1025	112	699	35	720	44
	(735)		792	107			572	64
	612				450			
	552	14	553	15	401	13	403	16
	366	15			355	15		
	202	(40)			210	(40)		
Ramano	3586							
	3408	70			2524			
	3276							
	3056	70			2284			
	550		· ·		398			

TABLE II. Infrared and Raman frequencies of crystalline HF and DF.

* $\beta_{1/2}$ is the full linewidth at half-intensity.

^b All infrared spectra recorded at T = -185 °C.

° All Raman samples grown from the melt. Spectra at T = -193 °C.

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centration of the guest isotope is increased by several percent, the intensity ratio of these lines to the strong singlet lines remains nearly constant, while the relative intensity of the pair lines increases sharply. The lines at 3490 and 2605 cm⁻¹ cannot, therefore, be part of the spectrum of triplets. quartets, etc., of solute molecules.

Infrared spectra of the librational region of films of HF and DF are shown in Figs. 7 and 8. There is a one-to-one correspondence between the number and shape of the HF and DF lines. (The sharp peak in the DF spectrum near 360 cm⁻¹ has its analog, shown elsewhere, in HF). The most striking feature of these spectra is the behavior of the 792 cm⁻¹ HF absorption with variation in deposition conditions. When the films are deposited near -120° C and subsequently cooled to -185° C, this peak is almost completely extinguished. The other librational lines are slightly sharper when films are prepared in this manner rather than by deposition directly at -185° C. Our spectra of films prepared in the latter fashion agree well with those of Sastri and Hornig⁴ and Hiebert,² but not with those of Giguère and Zengin.³

If the film is prepared by slow ($\sim 2 \text{ min}$) deposition at -185°C from a gas reservoir containing HF at 5-mm pressure, the spectrum in Fig. 9 is obtained. This is very similar to the results reported by Giguère and Zengin; here the 792-cm⁻¹ absorption has disappeared entirely, leaving a broad shoulder on the high-frequency side of the 550-cm⁻¹ peak. The halfwidths of the absorption peaks now are even greater than when the films are deposited in a burst at -185°C .

Qualitatively, the picture seems clear. The most nearly perfect crystals are formed when the vapor is



FIG. 7. Infrared spectra of librational region in HF.



FIG. 8. Infrared spectrum of librational region in DF.

deposited in a burst at temperatures near the melting point, so that a short-lived liquid film is possible. As the temperature of the substrate on which the vapor condenses is lowered, and as the deposition rate is decreased, the lifetime of this liquid film is decreased. A less-than-perfect crystalline film results. The data on the librations are summarized in Table II.

Far-infrared spectra of films of HF and DF deposited at -120° C are shown in Fig. 10. These are ratioed spectra obtained on the interferometer, and they are meaningful down to about 30 cm⁻¹. Two bands appear for both HF and DF, and these must be pseudotranslations, as indicated by the small dependence of their frequency on the hydrogen mass. The 366-cm⁻¹ HF band has been observed,²⁻⁴ but the 355-cm⁻¹ DF band has not. A peculiar behavior is the shift to *higher* frequency of the 202-cm⁻¹ HF band on deuteration. Similar behavior has been reported in HCl-DCl and HBr-DBr.⁹

Raman spectra of the lattice region reveal only one line for both HF and DF, and this only at the very limit of instrumental performance. The spectra are shown in Fig. 11, and the hashed region indicates the noise level.

III. DISCUSSION

A. Stretching Region

In the light of the present experimental evidence, the assignment of the two weak lines in the stretching region of either pure isotopic crystal becomes clear. The fact that the separation between either strong line and its higher-frequency satellite remains constant on

⁹ A. Anderson, H. A. Gebbie, and S. H. Walmsley, Mol. Phys. 7, 401 (1964).



FIG. 9. Infrared spectrum of a film of HF grown by very slow deposition. Librational region is shown.

deuteration suggests that we are observing combinations of the stretching components with a pseudotranslational lattice band near 200 cm⁻¹. This band is observed directly in the far infrared at 202 cm⁻¹ in HF and 210 cm⁻¹ in DF.

The dilute isotopic crystals were studied to ascertain whether the extra lines might arise from molecules on different sites. A very weak extra line is, in fact, noted at 3490 cm⁻¹ in dilute HF, but its frequency separation from the main singlet peak, 213 cm⁻¹, remains nearly constant in going to DF, where the line spacing in question is 201 cm⁻¹, rather than the value of 154 cm⁻¹ expected if the weak lines arise from molecules on different sites. Furthermore, the values inferred here by difference from the lattice frequencies of the *host* crystal, 213 cm⁻¹ for DF and 201 cm⁻¹ for HF, agree nicely with the values observed directly: 210 cm⁻¹ for DF and 202 cm⁻² for HF.

Of the two spectroscopically active stretching vibrations of an infinite zigzag chain of heteronuclear diatomic molecules, one is totally symmetric, i.e., all molecules stretch in phase. The other is the "antisymmetric" stretch, in which alternate molecules are exactly out of phase. Hornig and Osberg¹⁰ have shown that if the oscillating dipole moment is developed strictly along the figure axis of the molecule, then

$I_{\rm sym}/I_{\rm antisym} = \cot^2\beta$,

where β is the angle between any molecule and the crystallographic axis along the chain, and I_{sym} and $I_{antisym}$ refer to the infrared absorption intensity of the totally symmetric and antisymmetric vibration of the chain, respectively. The average value of the ratio of the intensity of the 3060-cm⁻¹ HF band to the intensity of the 3400-cm⁻¹ band is 2.4. This leads to $\beta \simeq 33^{\circ}$, in good agreement with the value of 30° obtained by x-ray methods for the FFF angle. More important, it is practically certain that the lower-frequency, more intense of the coupling components in either HF or DF

is the totally symmetric stretching vibration, and the higher-frequency component is the antisymmetric vibration.

An analogous expression can be derived for the relative intensity of the stretching components of the zigzag chain in the Raman spectrum. The derivation is given in Appendix I. The result is

$$R = \frac{I_{\rm sym}}{I_{\rm antisym}} = \frac{2a^2 + b^2 - 2(a-b)^2 \sin^2\!\beta \cos^2\!\beta}{2(a-b)^2 \sin^2\!\beta \cos^2\!\beta} ,$$

where and

$$b=d\alpha_{\rm H}/dQ,$$

 $a = d\alpha \mathbf{1}/dQ$,

b and a being the longitudinal and transverse molecular polarizability changes with respect to the stretching coordinate Q, respectively. This expression is derived for isotropic illumination of the sample, and specifically assumes cylindrical symmetry of the molecular polarizability tensor, in other words, the oriented gas model. Values of a and b for HF have been deduced by Oksengorn,¹¹ who finds a=0.107 Å²; b=1.96 Å². Using these values and $\beta = 30^{\circ}$ we obtain R = 2.0, which can be compared with the experimentally observed value for HF of 4.0 ± 1.0 . The experimental value corresponds to $\beta \simeq 21^{\circ}$. The agreement with simple theory is less satisfactory here than for the infrared case, but the assignment is confirmed: again the low-frequency component is the symmetric vibration and the high-frequency line arises from the antisymmetric mode. The calculated intensity ratios are for a C_{2v} two-molecule



FIG. 10. Far-infrared spectra of films of HF and DF.

¹¹ B. Oksengorn, Spectrochim. Acta 20, 99 (1964).

¹⁰ D. F. Hornig and W. E. Osberg, Jr., J. Chem. Phys. 23, 662 (1955),

unit cell. The addition of a second chain, either parallel or antiparallel, does not affect either the infrared or Raman result. In other words, the ratios are correct for either D_{2h}^{16} or D_{2h}^{17} .

B. Translational Vibrations

The two pseudotranslations can also be assigned in a relatively straightforward, if qualitative manner. The two translational vibrations of a planar zigzag chain which develop intensity in the infrared are the motions in which adjacent molecules beat against each other, the vibrations being polarized along the chain axis in one case, and perpendicular to it, but in the plane of the chain in the other. Since the hydrogen bands are inclined at approximately 30° to the chain axis, one might expect the force constant for translation along the chain axis to be substantially greater than that for the perpendicular vibration. This idea is borne out by comparison with the translational frequencies observed in HCl, HBr, and HI,9,12 where the observed lines approach each other in frequency as the chain angle approaches 45°. The 360-cm⁻¹ band is consequently assigned as the translation parallel to the chain axis, while the 200-cm⁻¹ transition is the fundamental of the perpendicular mode.

C. Librations

The three infrared-active librations of an infinite zigzag chain include two in-plane motions and an out-of-plane vibration. Of the in-plane vibrations, one is symmetric and the other antisymmetric with respect to the screw axis along the chain. If we adopt a model for the librational intensities in which nonpolarizable dipoles μ oscillate about their equilibrium positions, then the in-plane symmetric vibration has a net dipole moment change proportional to $2\mu \sin\beta$, while for the antisymmetric mode the change is proportional to $2\mu\cos\beta$. The out-of-plane libration is also antisymmetric with respect to the chain screw axis, so that the net dipole change is proportional to 2μ if the chain is planar. The relative intensities of these three absorptions, then, ought to stand in the ratios $1:\cos^2\beta:\sin^2\beta$, or 4:3:1 if $\beta = 30^{\circ}$. The out-of-plane libration is expected, therefore, to appear with an intensity equal to the sum of the intensities of the two in-plane librations, although the simple theory is correct only if the librational amplitude is the same in all vibrations. Furthermore, by the usual empirical rules¹³ the out-ofplane librations are expected at lower frequencies than in-plane motions.

The measured intensity ratio of the 962-cm⁻¹ HF peak to the 552-cm⁻¹ peak is 1.25, so it is tempting to assign the 552-cm⁻¹ line as the out-of-plane libration

FIG. 11. Raman spectra of a portion of the lattice 600 region of HF and DF.



and 962-cm⁻¹ line together with its shoulder near 1025 cm⁻¹ as the two in-plane librations. Alternatively, the 962-cm⁻¹ band might be the antisymmetric in-plane mode, and the 1200-cm⁻¹ band, the symmetric in-plane libration, although the agreement with the simple intensity rules would now be worse. Finally, one ought to consider the 792-cm⁻¹ HF band as the out-of-plane libration. If this is the case, then a perferential orientation of the sample which extinguishes this absorption would not affect any other absorption, since no other vibration polarized normal to the plane of the zigzag is infrared active. Because of its varied appearance under different preparation conditions, however, we believe that this absorption is not part of the spectrum of the stable, perfect crystal. The possibility that this is an absorption due to a second, metastable crystal phase seems unlikely: Only one phase of HF is known,14 and no changes in other regions of the spectrum other than line sharpening are observed under conditions which cause the line in question to vanish. With these several options it seems impossible to make any conclusive assignment, although we prefer the assignment of the 552-cm⁻¹ line as the out-of-plane libration, and of the lines at 962 and 1025 cm⁻¹ as the two inplane librations. The weak line at 612 cm⁻¹ in HF may be a Christiansen filter effect associated with the 552 cm^{-1} line, while the bands at 1100-1200 cm^{-1} may be overtones or combination bands.

D. Neutron-Scattering Results

Our assignment of the lattice modes observed in infrared differs somewhat from an assignment of frequencies observed in the inelastic neutron scattering spectrum.^{15,16} The spectrum of cold (40-cm⁻¹) neutrons which gain energy in scattering off crystalline HF contains maxima at 535 ± 16 and 53 ± 8 cm⁻¹, and a

¹² D. W. Robinson, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Paper 104, 1964. ¹³ G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, Calif., 1960).

¹⁴ J. H. Hu, D. White, and H. L. Johnston, J. Am. Chem. Soc. 75, 1232 (1953). ¹⁶ H. Boutin, G. J. Safford, and V. Brajovic, J. Chem. Phys.

^{39, 3135 (1963).}

¹⁶ H. Boutin and G. J. Safford, in Inelastic Scattering of Neutrons (International Atomic Energy Commission, Vienna, 1965), Vol. 2, p. 393.

ν (cm ⁻¹) ^a	$\Delta \nu \ (\mathrm{cm}^{-1})$	F_{ii} (mdyn/Å)	fij
$ \nu_{11}(R) = 3056 $ $ \nu_{22}(R) = 3408 $		5.265 6.546	$\begin{array}{c} f_0 = 5.903 \\ f_{12} = -0.629 \end{array}$
$\nu_{23}(ir) = 3400$ $\nu_{44}(ir) = 3061$		$6.518 \\ 5.283$	$\begin{array}{c} f_{13} = +0.003 \\ f_{14} = -0.012 \end{array}$

TABLE III. Force constants for stretching components in HF crystal.

^a R is Raman and ir is infrared.

shoulder near 218 ± 16 cm⁻¹. The 535- and 218-cm⁻¹ peaks probably correspond to the frequencies 552 and 202 cm⁻¹ observed in the infrared. Boutin and Safford have assigned the 535-cm⁻¹ band as "an optical mode involving the stretching of an FH-F link,"¹⁶ while the 218-cm⁻¹ shoulder was assigned as a "cooperative deformation" of the chain.¹⁶ From the simple fact that the 552-cm⁻¹ HF line observed in infrared or Raman shifts to 401 cm⁻¹ on deuteration, it is clear that the associated motion is a libration, not a hydrogen-bond stretch. This assignment is strengthened by the observation that the 535-cm⁻¹ neutron peak appears with enormous intensity. and therefore must be associated with a vibration in which the protons have large amplitude, in other words, a libration. The intensity of the shoulder observed in the neutron spectrum at 218⁻¹ is much lower, supporting our assignment of this line as an FH-F stretching or pseudotranslational vibration.

E. Force Constants and Structure

The only evidence obtained in this study which sheds light on the structural question is the coincidence or nonconcidence of the infrared and Raman lines. More conclusive evidence would be available if it had been possible to observe all of the Raman-active lattice modes, but we were not able to do this.

Before comparing infrared and Raman frequencies, it is necessary to take account of the fact that the infrared and Raman spectra were obtained on samples at different temperatures. Observation of the spectra in the stretching region at various temperatures between -160° and -190° C establishes that the temperature dependence of these frequencies, $d\nu/dT = 0.5 \pm$ 0.1 cm⁻¹/deg. Confining our attention to the HF frequencies observed at -185° C in infrared, we wish to correct these to -193 °C, the temperature at which the Raman data were obtained. The frequencies of the stretching vibrations of HF at -193° C are recorded in Table III. Within experimental error, the infrared and Raman lines are coincident in HF, and the values are even closer in DF. The experimental uncertainties, it ought to be remarked, are rather large because of the breadth of the lines, particularly in the Raman, where 10-cm⁻¹ slits had to be used. Consequently the small observed noncoincidence may be meaningful.

It is convenient to discuss the intermolecular forces in terms of force constants. Horning and Osberg¹⁰ have given the procedure for calculating stretching force constants for the hydrogen halides in their orthorhombic phase. For the D_{2h}^{16} , four-molecule primitive cell structure, the following symmetry coordinates are appropriate:

$$S_{1} = \frac{1}{2}(Q_{1} + Q_{2} + Q_{3} + Q_{4}),$$

$$S_{2} = \frac{1}{2}(Q_{1} - Q_{2} + Q_{3} - Q_{4}),$$

$$S_{3} = \frac{1}{2}(Q_{1} - Q_{2} - Q_{3} + Q_{4}),$$

$$S_{4} = \frac{1}{2}(Q_{1} + Q_{2} - Q_{3} - Q_{4}).$$

For the random structure D_{2h}^{17} , the primitive cell is isomorphous with C_{2v} and the symmetry coordinates are simply

$$\begin{split} S_1 &= 2^{-1/2} (Q_1 + Q_2), \\ S_2 &= 2^{-1/2} (Q_1 - Q_2). \end{split}$$

 Q_i is an internal coordinate corresponding to a change in bond length of the *i*th molecule. Using symmetry coordinates the secular determinant is easily factored yielding

$$\lambda_{ii} = 4\pi^2 c^2 \nu_{ii}^2 = G_{ii} F_{ii}.$$

For HF, the value of G_{ii} is the inverse reduced mass of the molecule, and ν_{ii} are the observed frequencies. The desired force constants, of which only four (for D_{2h} ¹⁶) are independent, can be expressed in terms of the symmetry force constants:

$$f_{0} = \frac{1}{4}(F_{11} + F_{22} + F_{33} + F_{44}),$$

$$f_{12} = f_{34} = \frac{1}{4}(F_{11} - F_{22} - F_{33} + F_{44}),$$

$$f_{13} = f_{24} = \frac{1}{4}(F_{11} + F_{22} - F_{33} - F_{44}),$$

$$f_{14} = f_{22} = \frac{1}{4}(F_{11} - F_{22} + F_{33} - F_{44}).$$

For D_{2h}^{17} the expressions are

$$f_0 = \frac{1}{2} (F_{11} + F_{22}),$$

$$f_{12} = \frac{1}{2} (F_{11} - F_{22}).$$

We designate the hydrogen-bonded pair of molecules in one chain as 1 and 2. Under D_{2h} ¹⁶ those in the antiparallel chain are 3 and 4, and Molecules 1 and 3, 2 and 4 are related by the center of inversion. The frequency numbering is given in Table III. This leads to the following set of force constants:

$$f_0 = 5.903 \text{ mdyn/Å},$$

$$f_{12} = -0.629,$$

$$f_{13} = +0.003,$$

$$f_{14} = -0.012.$$

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The two smaller constants go to zero, of course, if the infrared and Raman spectra are identically coincident. The small magnitude of f_{13} and f_{14} , $\frac{1}{200}$ th and $\frac{1}{50}$ th of f_{12} , respectively, suggests that they represent only experimental error, and that the crystal structure is D_{2h}^{17} . One would normally expect intermolecular forces between non-hydrogen-bonded molecules to be about $\frac{1}{10}$ th the strength of a hydrogen bond, although this argument is much too general to allow us to come to any firm conclusion on the structural question. More conclusive arguments based on comparison between theoretically calculated and experimental force constants will be published separately.

IV. CONCLUSION

On the basis of this work one can say with surety that the extra lines in the stretching region of HF or DF are combinations with a lattice vibration. The combination bands can also be identified in the spectrum of the guest molecule present at low concentrations in HF-DF mixed crystals. All of the observed transitions can be assigned with confidence, except for the librations, which are less certain. One of the librational bands is quite sensitive to the method of crystal preparation, and for this reason we believe it cannot be a librational fundamental of the stable, perfect crystal. Each Raman line is coincident within experimental error with an infrared line, which suggests that the crystal structure may be disordered in chain orientation.

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APPENDIX

In molecular coordinates the polarizability tensor for an HF molecule is cylindrical and diagonal, and is given by

$$\alpha = \begin{vmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{vmatrix}.$$

In some new coordinate system the polarizability tensor is

$$\alpha'=T\alpha T^{-1},$$

where T is a transformation matrix appropriate for a vector so that V' = TV, and $TT^{-1} = E$. For orthogonal

matrices such as these $T^{-1} = \tilde{T}$. For a planar twomolecule link of a zigzag chain, the appropriate matrices

$$T_{1} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\beta_{1} & -\sin\beta_{1} \\ 0 & \sin\beta_{1} & \cos\beta_{1} \end{vmatrix},$$
$$T_{2} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\beta_{2} & \sin\beta_{2} \\ 0 & -\sin\beta_{2} & \cos\beta_{2} \end{vmatrix}.$$

In crystal coordinates,

$$\begin{aligned} x_1' &= T_1 \alpha_1 \widetilde{T}_1 \\ &= \begin{vmatrix} a & 0 & 0 \\ 0 & b \cos^2 \beta_1 + a \sin^2 \beta_1 & (b-a) \sin \beta_1 \cos \beta_1 \\ 0 & (b-a) \sin \beta_1 \cos \beta_1 & b \sin^2 \beta_1 + a \cos^2 \beta_1 \end{vmatrix}, \end{aligned}$$

 $\alpha_2' = T_2 \alpha_2 \tilde{T}_2$

$$= \begin{vmatrix} a & 0 & 0 \\ 0 & b\cos^2\beta_2 + a\sin^2\beta_2 & (a-b)\sin\beta_2\cos\beta_2 \\ 0 & (a-b)\sin\beta_2\cos\beta_2 & b\sin^2\beta_2 + a\cos^2\beta_2 \end{vmatrix}$$

where $\alpha_1 = \alpha_2 = \alpha$.

Now if we assume additive polarizabilities

$$\alpha_u = \alpha_1' Q_1 + \alpha_2' Q_2,$$

and α_u is the polarizability tensor for the unit cell. Using the symmetry coordinates appropriate for the two-molecule unit cell we find

$$Q_1 = 2^{-1/2} (S_1 + S_2),$$

$$Q_2 = 2^{-1/2} (S_1 - S_2).$$

Then

$$\begin{aligned} \alpha_{u} &= \begin{vmatrix} a & 0 & 0 \\ 0 & a\sin^{2}\beta + b\cos^{2}\beta & 0 \\ 0 & 0 & a\cos^{2}\beta + b\sin^{2}\beta \end{vmatrix} & 2^{-1/2}S_{1} \\ &+ \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & (b-a)\sin\beta\cos\beta \\ 0 & (b-a)\sin\beta\cos\beta & 0 \end{vmatrix} & 2^{-1/2}S_{2}, \end{aligned}$$

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$$\alpha_{u} = \begin{vmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{vmatrix} 2^{-1/2} S_{1} + \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & D \\ 0 & D & 0 \end{vmatrix} 2^{-1/2} S_{2},$$

where $\beta = |\beta_1| = |\beta_2|$.

Given α_u , the relative intensities may be calculated by averaging over the angles of illumination and observation appropriate to a given experiment.¹⁷ The ¹⁷ S. Bhagavantam, Scattering of Light and the Raman Effect (Chemical Publ. Co., Brooklyn, N.Y., 1942). case where illumination is isotropic and only light scattered along a single laboratory axis is collected is particularly simple. This is also appropriate for the experiments described above. In this case we find

$$R = 5(A^2 + B^2 + C^2)/10D^2$$
,

$$R = \frac{2a^2 + b^2 - 2(a-b)^2 \cos^2\beta \sin^2\beta}{2(a-b)^2 \cos^2\beta \sin^2\beta},$$

where R is defined above.

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Fundamental Equations of Electrochemical Kinetics at Porous Gas-Diffusion Electrodes

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The kinetics of a charge-transfer reaction at a porous gas-diffusion electrode are presented using the simple pore model. The rate of diffusion of the reactant gas through the electrolyte-free part of the pore is sufficiently fast for pore radii of 10⁻⁴ cm or higher. The dissolution of gas at the gas-electrolyte interface causes no limitations. For the processes occurring in the electrolyte occupied part of the pore, all forms of polarization are taken into account and expressions are derived for the current distribution and overpotential-current-density relations. By using numerical values of the various parameters (diffusion coefficient, solubility of reactant gas in electrolyte, specific conductance of electrolyte), it is shown that the case of all forms of polarization reduces to one of activation and concentration overpotential. A one-dimensional treatment is valid up to about 25% of the limiting current for this case. The dependence of current-distribution and overpotential-current-density relations on the various kinetic parameters is shown graphically for these cases. It is shown that most of the current (over 90%) is generated over a small fraction of the pore length $(10^{-2}-10^{-4})$ in the practical overpotential range (i.e., for reasonable current densities) when all forms of polarization are taken into account. The case of activation and ohmic overpotential shows the interesting result that current densities can be increased by a factor of up to 10³ times if concentration overpotential is eliminated, as for example by using very soluble fuels or by circulating the electrolyte saturated with reactant through the porous electrode.

I. INTRODUCTION

CEVERAL papers have appeared in the literature on D theories of porous electrodes. A majority of them consider two-phase systems, which are thus applicable only to redox systems.1-3 Of the few which deal with porous gas-diffusion electrodes, the theories do not generally take into account all forms of polarization

losses simultaneously.^{4–8} In addition, the effects of the kinetic and physical parameters on the currentdensity-overpotential and current-distribution relations are not clearly seen in the previously published work.

These problems are considered in the present paper using the simple pore model.⁴ The thin-film model is treated in a subsequent paper.9 These two models

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