Pressure effects on Raman scattering from solid HF and DF

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Single-crystal samples of HF and DF have been studied by Raman spectroscopy in a diamond-anvil cell up to pressures of about 12 GPa. Two translational, three librational, and two stretching modes were studied as a function of pressure. Comparison of the librational-mode frequencies in HF and DF using the expected isotope ratio has allowed the identification of one strong and two weak fundamental librational modes in HF and DF. This resolves some of the confusion in earlier studies on HF and DF. There is some evidence for a transition to a symmetric hydrogen-bonded phase in HF at about 6 GPa. There was no evidence for this transition in DF up to 12 GPa. An analysis of the pressure dependence of the symmetric-stretching modes in HF and DF has been done using the double-well model of Jansen et al. [Phys. Rev. B **35**, 9830 (1987)] along with perturbation theory to give estimates of the pressure dependence of the barrier height.

I. INTRODUCTION

The studies presented here on solid hydrogen fluoride are the results of experiments that form part of a general study of hydrogen bonding. Hydrogen fluoride (HF) has been chosen for study because it is one of the most basic hydrogen-bonded materials. The dynamical and structural properties of crystals of solid hydrogen fluoride (HF) and its isomorph deuterium fluoride (DF) are studied as a function of pressure. The hydrogen fluoride crystals have molecules arranged in zig-zag chains aligned in planes. In the chain each molecule is hydrogen bonded to its two nearest neighbors while bonds to molecules in neighboring chains arise from weaker Van der Waals interactions. The hydrogen bonds (H bonds) in HF are among the strongest known. Hydrogen bonding should dominate the intermolecular interactions in this quasi-one-dimensional structure and is expected to strengthen as the length of the hydrogen bond is shortened. By exerting pressure on the samples of HF and DF the volume can be changed resulting in a corresponding shortening of the interatomic distances. In the experiments reported here, pressure was applied by the use of a diamond-anvil cell (DAC). The sample is contained between two diamonds whose transparency allows the use of x-ray, infrared, Brillouin, and Raman spectroscopy to study the structure and dynamics of the sample over a range of pressures. We have previously published the results of our Brillouin studies on single-crystal samples of HF as a function of pressure.[1]

A. Pressure studies on hydrogen-bonded solids

In recent years several of the classic hydrogen-bonded solids have been studied as a function of pressure. A great amount of research has been done on the three-dimensional hydrogen-bonded structure of solid H_2O. Recent Raman and x-ray studies of ice VII (Ref. 2) showed a strong decrease in the O—H stretching frequency as well as evidence for increasing O—H bond length for decreasing O-O distance. Infrared data of the uncoupled O—H stretch in ice VII (Ref. 3) showed that the effective charge of the O—H stretch increased with increasing pressure while at the same time the frequency of the O—H stretch decreased. Raman spectra of ice VIII (Ref. 4) up to 50 GPa have exhibited several characteristics interpreted as evidence of formation of the symmetric hydrogen bond structure, ice X. Further support for a transition to the ice X phase is observed in data from Brillouin experiments on ice VII (Ref. 5) which show a discontinuity in the elastic modulus of ice as a function of density at a pressure of 44 GPa. A high-pressure Raman study of NH_3 (Ref. 6) indicates a symmetrization of the H bonds of ammonia may occur at about 60 GPa.

Katz[7] and Johannsen et al.[8] have studied solid hydrogen bromide (HBr) and hydrogen chloride (HCl) at high pressure. The low-temperature phase III of both of these materials is structurally isomorphic to the one known solid phase of HF. A strong decrease in stretching frequency with increasing pressure was seen in both studies. These studies have also obtained lattice parameters of HBr as a function of pressure. The data show that the stretching frequency of HBr is a nonlinear function of the Br-Br distance in the chain, in contrast with the linear decrease of the stretching frequency as a function of pressure. The stretching-mode behavior should indicate approach to a transition similar to that seen in ice X. Johannsen et al. have observed in their Raman spectra evidence of a transition in HBr from the C_{2v}^{12} ($Cmc2_1$) structure to a symmetric phase with the D_{2h}^{17} ($Cmcm$) structure at a pressure of 32 GPa. At this pressure both stretching modes have disappeared, and the lattice-mode region has changed to three different modes. The spectrum observed is compatible with the expected spectrum for the symmetric structure. In HCl the stretching frequencies do not decrease as strongly as in HBr and there is no evidence of a phase transition up to 48 GPa. A similar transition is expected in HF and is one of the objectives of this study. In the data reported below for HF some evidence is seen for a similar phase transition.

B. Previous studies on solid HF

The crystal structure of HF has been studied using x-ray diffraction methods by Atoji and Lipscomb.[9] The results of a neutron-diffraction study of DF by Johnson, Sandor, and Arzi,[10] are now generally accepted as the definitive work in the determination of the structure of HF and DF. Their data indicated solid HF crystallizes in the C_{2v}^{12} ($Bm2_1b$) for HF structure with parallel zig-zag hydrogen-bonded chains.

Many infrared, Raman, and inelastic neutron-scattering experiments have been reported on HF and DF. Early studies by Guigere and Zengin[11] and by Hornig's group[12,13] as well as an inelastic neutron study by Boutin et al.[14] were not able to be reconciled with the early structural proposals for HF. Sastri and Hornig[12] found that the ratio of the frequency splitting of the stretching modes of HF to the frequency splitting of the stretching modes in DF was 1.46. This is very different than the expected square root of the ratio of the reduced masses, 1.38. The coincidence of infrared and Raman lines in the spectra obtained by Kittelberger and Horning[13] ruled out the D_{2h}^{16} ($Pmnb$) antiparallel chain structure and gave evidence for either the disordered D_{2h}^{17} structure or the C_{2v}^{12} parallel chain structure.

The Raman studies of Anderson et al.[15] provided further support for the C_{2v}^{12} structure with tentative identification of all of the nine Raman active modes expected. They made symmetry assignments of all these modes.

In the translational region there is general agreement on the mode assignments. We shall refer to the peak positions as determined by Anderson et al. unless otherwise referenced. The lowest-lying translational mode, at 56 cm^{-1} in HF and DF, was determined to have A_2 symmetry since it had not been seen in any of the infrared work.

The highest-frequency mode in the translational region, at 364 cm^{-1} in HF and 358 cm^{-1} in DF, was assigned B_1 symmetry since this symmetry involves vibration of adjacent molecules along the chain direction. This is the so-called hydrogen-bond mode. The intermediate frequency mode, at 188 cm^{-1} in HF and 189 cm^{-1} in DF, is then assigned the A_1 symmetry which is the vibration in the plane of the chain with the motion being perpendicular to the chain direction.

In the librational region four modes are predicted for the C_{2v}^{12} crystal structure of HF and DF. These are A_1, A_2 B_1, and B_2. There continues to be considerable disagreement among the different groups who have studied the vibrational spectra of solid HF and DF on both the identification of the fundamental modes and the symmetry assignments in the librational region. The results of the earlier studies of Hornig's group[12,13] settled on three peaks at 550, 965, and 1025 cm^{-1} in the HF librational region as the fundamental vibrations. These peaks were given B_2-, B_1-, and A_1-symmetry assignment, respectively. For DF the corresponding results are 403 and 720 cm^{-1} with no peak corresponding to the highest-frequency libration in HF. Anderson et al. make tentative assignments for the four modes predicted, A_1, A_2, B_1, and B_2 at 569.5, 687, 742, and 943 cm^{-1}, respectively, in HF. The corresponding assignments in DF were at 416.5, 491, 551.5, and 703 cm^{-1}. The peak at 569 cm^{-1} in the data of Anderson et. al. is thought to correspond to the peak at 550 cm^{-1} in the infrared work[13] which is consistent with the A_1 assignment. In the experimental section of the present work we will show that some of the features identified above are probably not fundamental vibrations and that the broad 742-cm^{-1} feature is in fact two peaks that are seen better in the higher-pressure spectra.

In the stretching region four modes are observed, one

TABLE I. Experimental spectroscopic data for solid HF and DF at ambient pressure. The vibrational-mode frequencies listed were determined by ir and Raman spectroscopy. All values are in cm^{-1}. T stands for translation, L for libration, S for stretching, and C for combination.

Mode	Anderson et al.[a]		Kittelberger and Hornig[b]	
	HF	DF	HF	DF
A_2 T	56	56		
A_1 T	188	189	202	210
B_1 T	364	358	366	355
Unassigned	548			
A_1 L	569	416	962	699
A_2 L	678	486		
B_1 L	745	543	1025	
Unassigned			792	572
B_2 L	943	696	552	401
C 2(A_1 L)	1127	822	1133	855
C 2(A_1 L)	1177	868	1200	900
A_1 S	3045	2286	3065	2292
C (A_1 S+A_1 T)	3265	2479	3275	2495
B_1 S	3386	2513	3404	2526
C (B_1 S+A_1 T)	3586	2711	3585	2712

[a]Reference 15.
[b]Reference 13.

strong- and one medium-intensity peak, each with a weak feature on its high-frequency side. There is general agreement that the lowest-frequency mode observed in this region is the A_1 symmetric-stretching mode and the medium-intensity peak is the B_1 antisymmetric-stretching mode. The remaining two peaks were determined to be combinations of the A_1 translational mode with the two stretching modes. Table I summarizes the spectroscopic data for solid HF and DF at zero pressure.

The HF molecule as well as polymers(dimers, trimers, etc.), and the HF infinite chain have been attractive as a testing grounds for several quantum-mechanical molecular electronic calculations. The appeal of HF for these calculations is due to the fundamental nature of the hydrogen bond in HF and because the small number of electrons makes all electron calculations feasible. We mention only a few of the many calculations that have been done. The papers give reference to the other studies. Zunger[16] calculated electronic properties of some high-symmetry points in the Brillouin zone (BZ) of an infinite solid using one-electron energy levels of a finite periodic structure. A semiempirical linear combination of atomic orbitals (LCAO) method was used to obtain the one-electron energy spectrum. The results show that the H—F bond distance, R_{HF}, should increase as the F—F bond distance, R_{FF}, decreases. The results also indicate a symmetric hydrogen-bond formation at a value of 2.3 Å for R_{FF}. Ab initio crystal-orbital calculations performed on an infinite linear chain of HF and molecular-orbital (MO) calculations on the HF monomer and dimer by Karpfen and Schuster[17] and by Karpfen[18] showed basic agreement with the experimental values. An improved agreement between calculated and observed structures as well as calculation of a potential-energy surface including assignments of vibrational-mode frequencies was obtained with an ab initio crystal-orbital calculation on an infinite bent chain by Beyer and Karpfen.[19] The vibrational-mode assignments made by Beyer and Karpfen are reasonably certain and agree with Anderson et al. except for the confusion that is still evident in the librational region.

Recent calculations of the electronic structure and of the potential energy for hydrogen motion in the A_1 stretching mode in solid HF have been presented by Jansen et al.[20] Ab initio calculations are done on a ring-structure H_6F_6 molecule with C_{6n} symmetry. A qualitative model based on a double-well potential was developed for the pressure dependence of the symmetric-stretching mode. This model will be used to interpret the A_1 stretching-mode data of the Raman spectra presented in this paper. Another calculation has recently been presented by Springborg[21] using a density-functional formalism on a bent HF chain. The results give good agreement on the bond length and the stretching mode frequency at zero pressure.

Solid HF has also been a popular structure for vibrational lattice-dynamical calculations. Since there are only two molecules per unit cell and two atoms per molecule the number of force constants needed to describe the system remains small. Additionally, many calculations include only an isolated chain, further simplifying the

procedure. Since unambiguous identification of all of the fundamental vibrations for the C_{2v}^{12} structure has not been made, the usefulness of the results of these calculations remains unclear. Tubino and Zerbi[22] used a single-chain model and fit a seven-parameter force field, within the harmonic approximation, to the experimental values for the $k=0$ modes obtained by Kittleberger and Hornig.[13] Axman et al.[23] used a three-dimensional model employing interactions between nearest and next-nearest fluorine atoms (F atoms) in adjacent chains. The intrachain force constants were fit to the $k=0$ experimental frequencies. The interchain force constants were used to vary the maxima in the density of states to fit their inelastic neutron scattering measurements. Beyer and Karpfen fit data from their energy-surface calculation to obtain force constants and mode frequencies which gave qualitative agreement with experimental results. Their results differ from the other calculations discussed here since they have not fit parameters to agree with the (presumably incorrectly identified) observed frequencies. Anderson et al.[24] use a single-chain model with four spring-type force constants and obtain a reasonable qualitative agreement with the experimental results except that they assign A_2 symmetry to the strong infrared-active librational mode at 569 cm^{-1}, which is a change from the A_1 assignment in their earlier experimental paper. This assignment is probably incorrect since modes with A_2 symmetry are not infrared active. Higgs et al.[25] use a method similar to Anderson et al. with eight spring-type force constants including interchain forces. This calculation has the same problem with the A_2 assignment of the strong 569-cm^{-1} mode.

The studies to be presented here represent the first Raman work at high pressure on HF and DF. Section II describes the preparation of single-crystal samples of HF and DF used in the experiments. Section III gives the results of our Raman scattering experiments including the evidence we have for a transition to a symmetric hydrogen bond in HF (but not in DF). Section IV gives an analysis of the symmetric stretching-mode frequencies in HF and DF in terms of a double-potential-well model of the form discussed in Jansen et al.

II. EXPERIMENT

Samples of HF and DF were prepared in Merrill-Bassett[26] diamond-anvil cells. Because of the corrosive nature of HF, the normal gasket materials (Inconel X750 and T301 stainless steel) were lined with platinum. This was done by placing a small piece of platinum over the predrilled hole in the gasket. After this the gasket was repressed to the same thickness as before. The platinum became cold welded to the original gasket material during this second pressing process to provide a corrosion resistant lining. A somewhat smaller hole was then drilled in the center of this platinum plug.

Anhydrous HF and DF were obtained in lecture bottles from Matheson and Ozark Mahoning, respectively. H_2 and any other noncondensible impurities were removed by immersing the lecture bottle in liquid nitrogen

and then pumping with a mechanical pump. (Note the cooling of ordinary lecture bottles to these temperatures is not a recommended procedure because of the brittleness of carbon steels at low temperature.) HF or DF gas was then frozen into ice in a polyethylene U tube. A small flake of this ice was placed over the hole in the gasket of the diamond cell in a liquid-nitrogen bath. The cell was closed and tightened before warming to room temperature.

This loading procedure produced a fine-grained polycrystalline solid sample. The sample was then grown into either a single crystal or a few large crystals for the experiments. Crystal growth was facilitated by maintaining a sample temperature in the range 30–90 °C. Crystals were grown by changing the pressure and temperature of the sample until only a small seed crystal remained unmelted. The pressure and temperature were than adjusted so that the seed crystal grew into one single crystal which filled the sample volume. Sample growth was observed under a microscope through crossed polarizers and correlated with x-ray diffraction studies to determine the crystal orientation. The orientation of two crystal axes was determined directly by observation of a minimum of transmitted light through crossed polarizers. The x-ray diffraction experiments showed that the crystals almost always grew with the initial growth along the b axis in the plane of the diamond face. The growth in this direction was fast and fingerlike. This growth habit is not surprising since the intermolecular bonding in this direction is due to the strong hydrogen bonding. The second phase in the growth process consisted of the growth of a very than layer which covered the complete hole in the gasket. The thinness of the layer was evidenced by strong interference colors during this phase. X-ray diffraction established that this second growth was in the a direction. The final growth process was a thickening along the c axis in the direction perpendicular to the diamond faces. Many orders of interference colors were observed in this final growth phase.

The HF Raman spectra were taken in conventional near-backscattering geometry using a Spex 1403 double monochromator. The DF spectra were taken using a Spex 1402 double monochromator. The spectra taken on DF were done with the exciting laser beam incident at a 45° angle with respect to backscattering in order to minimize background scattering. Spatial filtering of the scattered light was used in the DF experiments in order to minimize diamond second-order Raman scattering and fluorescence. Both experiments were generally done at approximately 25 K with the sample mounted in a Displex cryogenic refrigerator. This low temperature is necessary because all of the modes, and particularly the stretching modes, broaden strongly with temperature.

The experiments reported here are limited to the pressure range up to 17 GPa at the highest and in most cases up to 12 GPa or lower. This limit is set by fracturing of the crystals which in turn makes the Raman signals unobservable. The anisotropy in the crystal growth mentioned above shows up in anisotropic deformation of the gasket hole as the pressure increases. Characteristic diagonal cracks relative to the b axis appear as the pressure

is raised above about 7 GPa. In the pressure range of 10–12 GPa, the amount of cracking becomes so large so that no clear area can be found and no useable Raman signals could be observed. One HF sample was raised to a pressure of 17 GPa at low temperature before the amount of breakup prevented further study at higher pressure. The strength of the Raman signals does not appear to decrease as the pressure increases. However, the intensity data are difficult to measure very accurately due to pressure broadening and variations in diamond fluorescence in different experimental runs. It is also difficult to compare the DF data to the HF data since the experimental setup was quite different in the two different experiments. The intensities of the spectra presented here have been scaled for clarity of presentation, so one should not attempt to derive any significance in relative intensities between spectra from different experimental runs. The quality of the Raman data presented here is somewhat less than ideal but represents considerable effort on these very weak scatterers.

Raman spectra were excited with the 488.0- and 514.5-nm lines of an argon-ion laser. The incident laser power was typically 0.2–0.4 W. The spectra obtained from DF showed much less ambiguity as to the identification of Raman peaks than that from HF especially in the librational region. The spectra of HF were plagued by the appearance of unidentifiable extra features in the librational region and a strong low-frequency background due to elastic scattering of the incident beam in the translational-mode region.

III. RESULTS AND DISCUSSION

A. Translational modes

Figure 1 shows Raman spectra for the translational region in HF and DF at similar pressures. In this region two modes were detected in the DF spectra. These modes have been assigned as the A_2 out-of-plane and A_1 in-plane translational modes by extrapolating the pressure dependence of the observed frequencies and comparing to the earlier work of Anderson et al. These extrapolations agree very well. The translational-mode HF spectra (but not the DF spectra) presented here are the logarithm of the intensity. In the HF spectra only the A_1 mode could be unambiguously observed. The A_2 mode was not seen due to very strong background scattering at low frequency. As expected there is negligible isotope effect for modes involving motion of the whole molecule. The very weak translational mode identified as the B_1 translation along the chain axis by Anderson et al. was not seen. The pressure dependence of the translational-mode frequencies in both HF and DF is shown in Fig. 2, and the results of linear least-squares fits to this data are given in Table II.

B. Librational modes

Figure 3 shows Raman spectra for the librational region in DF at several pressures. In the librational region of DF, three of the four modes predicted for the C_{2v}^{12} structure were observed and no other spectral features
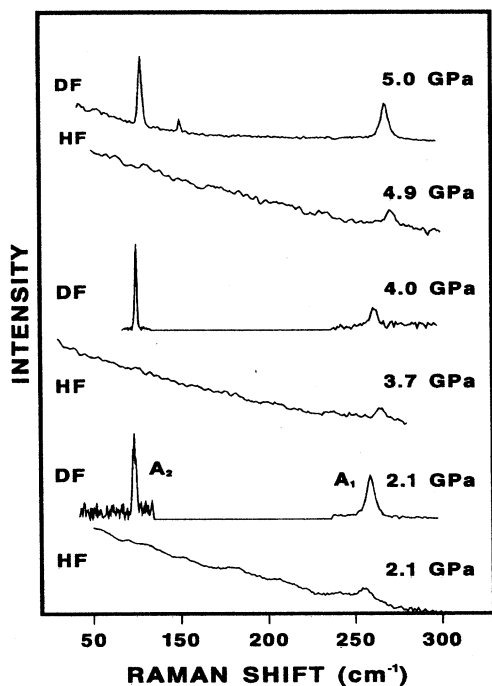
FIG. 1. Raman spectra for the translational-mode region of solid HF and DF at similar pressures. Because of the strong low-frequency background, the HF spectra presented are the logrithim of the intensity. In DF both the A_2 and A_1 modes are seen while only the A_1 mode was seen in HF due to the strong background and different experimental setup.
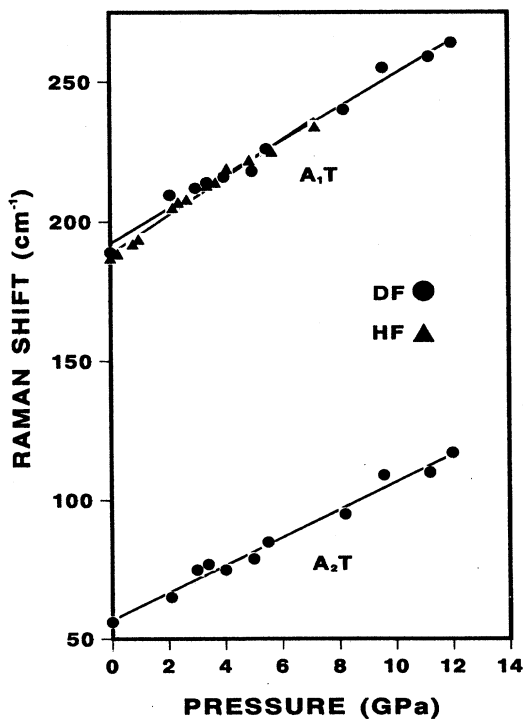
TABLE II. Results of linear regression fits of experimental Raman mode frequencies vs pressure for solid HF and DF at 25 K. The Raman frequency is given by $v(cm^{-1})=a+bP$ where P is the pressure in GPa.

Type	Mode	Material	a (cm^{-1})	b (cm^{-1}/GPa)
Translation	A_2	DF	58±2	4.8±0.3
	A_1	DF	192±2	6.0±0.3
		HF	188±2	6.8±0.3
Libration	$L1$	DF	409±3	5.6±0.5
		HF	566±1	6.2±0.4
	$L2$	DF	515±3	10.0±0.5
		HF	722±1	13.6±0.3
	$L3$	DF	564±4	9.6±0.6
		HF	776±2	12.8±0.6
Stretching	A_1	DF	2272±6	−33±1
		HF	3027±6	−54±2
	B_1	DF	2506±4	−21±1
		HF	3376±5	−32±2

caused confusion. The symmetry assignments of these modes are not clear and so here they are labeled $L1$, $L2$, and $L3$ in order of increasing frequency. We will discuss the symmetry assignments below. The $L1$ mode is the sharp, intense mode. The positions of the two weak features are designated $L2$ and $L3$. The intensities in the region of the spectra containing these peaks have been multiplied by a factor of approximately 3 relative to the region of the $L1$ peak in order to make these more clear.

FIG. 2. The pressure dependence of the A_2 and A_1 translational-mode frequencies in solid DF and the A_1 mode in solid HF. The lines are linear regression fits.
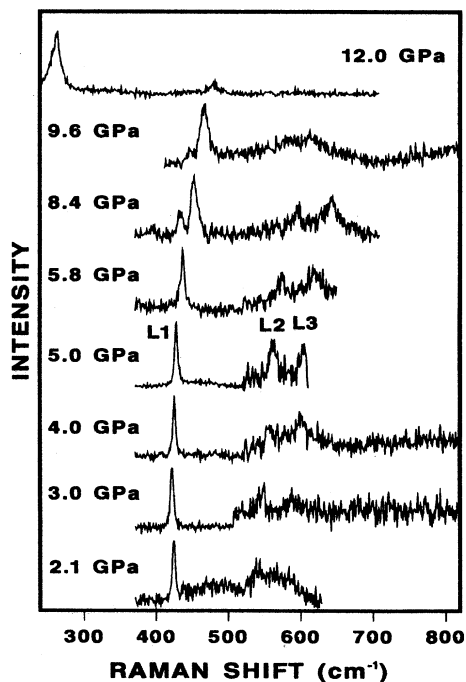

FIG. 3. Raman spectra for the librational region in DF at several pressures. The $L1$ mode is the sharp intense peak. The position of the two weak peaks, $L2$ and $L3$, are indicated. The intensities in the region beyond about 500 cm^{-1} have been multiplied by three for clarity. The peak at the low-frequency end of the 12-GPa spectra is the A_1 translational mode.

Figure 4 shows the Raman spectra for the librational region of HF for pressures between 0 and 4.9 GPa, while Fig. 5 shows this region for the pressure range of 2.7–17.6 GPa. As can be easily seen, these spectra are much more complicated than the corresponding spectra for DF. These experiments are the results of studies on three samples of HF. They need repetition but are presented here because they represent the best available spectra at the present time. In order to present a clear comparison of this region for both HF and DF, librational spectra for both materials at comparable pressures are shown in Fig. 6. The scale for the DF frequencies is smaller than the scale for the HF frequencies by a factor of 1.38 which is $(\mu_{DF}/\mu_{HF})^{1/2}$. In all of these figures, the HF librational spectra have been adjusted by the subtraction of a linear function to correct for the fluorescence background due to the diamonds. This adjustment was not necessary for the DF spectra.

In the HF librational spectra for the pressure range 0.8–5.7 GPa there are three peaks observed at the expected 1.38 factor times the corresponding DF librational frequencies. As a result of this correspondence these three peaks were identified as fundamental vibrations in HF as well as in DF and are given the same labels, $L1$, $L2$, and $L3$. The $L2$ and $L3$ peaks in HF, although weak, are of comparable intensity to the $L2$ and $L3$ peaks in DF. However, they are obviously much weaker than other features which appeared in the HF spectra in this region. Extrapolation of the pressure dependence of the $L1$ mode frequency shows that this mode correlates to the strong librational mode observed at 567 cm^{-1} in HF and 416
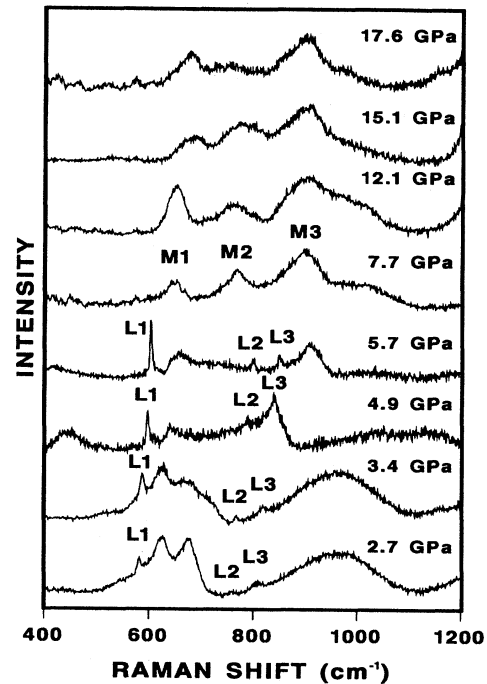

FIG. 5. Raman spectra for the librational region of HF for the pressure range of 2.7–17.6 GPa. The spectra for pressure up to 4.9 GPa are identical to Fig. 4. The positions of the $L1$, $L2$, and $L3$ fundamental modes are indicated. The spectra for 7.7 GPa and higher are qualitatively different showing three modes $M1$, $M2$, and $M3$. This suggests that a transition to the symmetric hydrogen-bond D_{2h}^{17} structure has occurred. See text.
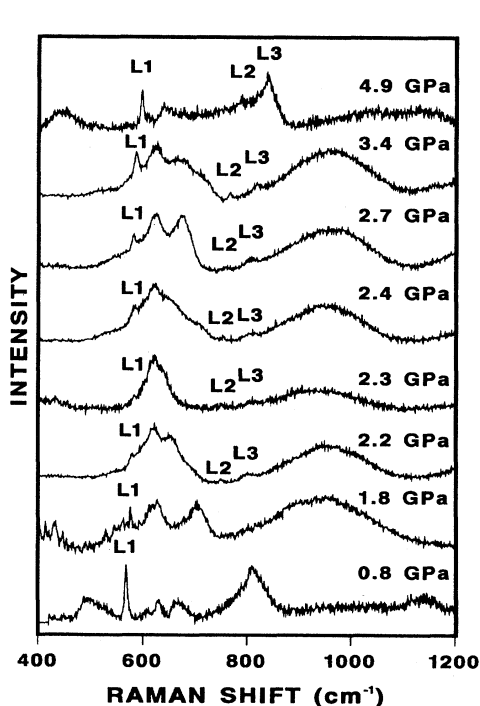

FIG. 4. Raman spectra for the librational region of HF for pressures between 0.8 and 4.9 GPa. The $L1$, $L2$, and $L3$ fundamental modes are indicated.
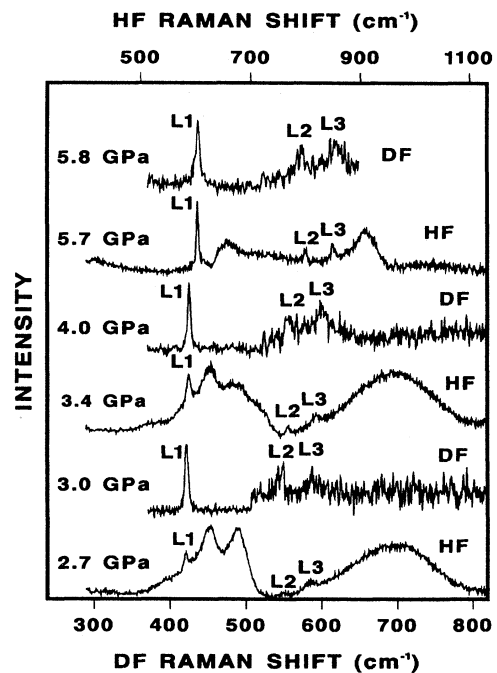

FIG. 6. Raman spectra in the librational region for HF and DF at comparable pressures showing the correspondence between the $L1$, $L2$, and $L3$ fundamental modes. The HF and DF frequency scales are related by a factor of 1.38. See text.

cm^{-1} in DF by Anderson et al. and to the strong narrow peaks seen in the infrared at 552 and 401 cm^{-1} in HF and DF by Kittelberger and Hornig. The $L1$ peak in HF seems to become nearly lost in the large structure just at higher frequencies in the spectra in the 2.2–2.7 GPa range. It then clearly reappears for the spectra between 3.4 and 5.7 GPa. At 7.7 GPa and higher the $L1$ peak has disappeared. Extrapolating the pressure dependence of the two weak higher-frequency librations, $L2$ and $L3$, to zero pressure and comparing with the earlier work of Anderson et al. shows that the broad but weak peak that they see at 742 cm^{-1} in HF and 551 cm^{-1} in DF actually consists of the two peaks, $L2$, and $L3$, which are seen as such as the pressure is raised. Figure 7 shows the pressure dependence of the $L1$, $L2$, and $L3$ librational-mode frequencies in both HF and DF and the pressure dependence of the new modes, $M1$, $M2$, and $M3$ in HF. The close agreement of the librational frequencies for HF and DF to the expected 1.38 factor indicates that these modes are quite harmonic. The results of regression fits to these data are given in Table II.

1. A possible symmetric hydrogen-bonded phase in HF

As seen in Fig. 6, the librational Raman spectra for HF above 5.7 GPa shows a distinct change in appearance. From 7.7 to 17.6 GPa the librational region for HF shows three broad peaks which have very little pressure
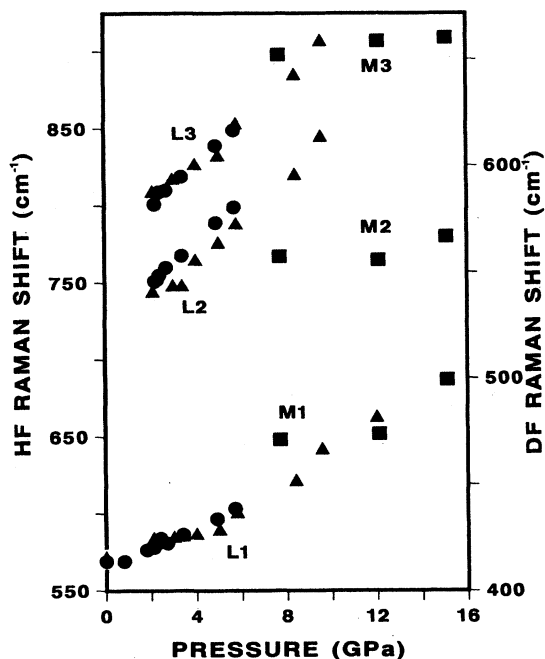

FIG. 7. Pressure dependence of the librational-mode frequencies in HF and DF. The $L1$, $L2$, and $L3$, modes in the C_{2v}^{12} structure of DF (solid triangles) and HF (solid circles) are shown. The points above 7 GPa for HF (solid squares) are for the three new modes, $M1$, $M2$, and $M3$, of the proposed D_{2h}^{17} structure. The HF frequency scale is 1.38 times the DF frequency scale.

dependence. These three peaks are designated $M1$, $M2$, and $M3$. Also there seem to be no observable features in the translational and stretching region for this range of pressure. Some characteristic changes in the Raman spectrum are expected in a phase transition from the C_{2v}^{12} structure to the D_{2h}^{17} structure. In the D_{2h}^{17} structure only three Raman active modes all due to the motion of F atoms are expected. These modes would be of symmetry A_g, B_{1g}, and B_{2g}. Because the hydrogen atoms are at centers of symmetry, none of the modes involving hydrogen-atom motion are Raman active. As was noted in the Introduction, this sort of transition has been observed in HBr by Johannsen et al.[8] The pressure dependence of the modes in librational region for both HF and DF are shown in Fig. 7. The three new modes in HF above 7 GPa, $M1$, $M2$, and $M3$, are indicated by a different symbol than the librational modes $L1$, $L2$, and $L3$ which occur at lower pressures. It should be noted that no evidence for such a symmetrizing phase transition was observed in DF up to 12 GPa. Because of the difficulties with the data in the translational and librational region, the HF experiments need to be repeated with the improved scattering geometry and collection optics before this proposed phase transition can be identified with certainty.

2. Symmetry assignments of librational modes in C_{2v}^{12} structure

As mentioned in the Introduction, there continues to be disagreement in the literature on both the identification as well as the symmetry assignments of the librational modes the normal phase of HF and DF. The $L1$ mode that we observe seems to give a very strong signal for all Raman studies done on HF and DF independent of the experimental geometry and sample preparation. We make the assignment for the $L1$ mode as having A_1 symmetry based on the identification of this mode with the strong infrared absorption peaks seen by Kittelberg and Hornig at approximately the same frequency. The earlier assignments of this peak as an (infrared inactive) A_2 mode must be incorrect.

In the earlier infrared studies of Kittelberger and Hornig[12] a peak was seen at 792 cm^{-1} in HF and 572 cm^{-1} in DF when the sample formed from gas deposited on the cell windows at $-185\,^{\circ}C$. When the sample was formed from gas deposited at $-125\,^{\circ}C$ this peak had almost completely disappeared. Kittelberger and Hornig[13] suggested two explanations for this effect. One interpretation suggested is the preferential orientation of the sample when it is prepared by condensation at temperatures near the melting point. If the sample forms in a single crystal with preferred orientation, it is possible that some modes will not be seen because of polarization selection rule effects. The other suggestion which was preferred by these authors is that an imperfect crystal is formed when the HF gas is deposited from the vapor at temperatures well below the melting point and the peak is seen due to a breakdown in translational symmetry. We feel that the most likely explanation, in view of the observation of the morphology of crystal growth in the diamond-anvil cell

described in the present work, is that a liquid film exists for a short time and large crystallites, with the b-a plane in the plane of the condensing surface formed on the window in their experiment. This orientation would prevent the observation of an infrared mode polarized along the c axis. For the C_{2v}^{12} structure the B_1 librational mode would be polarized along the c axis. We thus conclude that the infrared mode observed by Kittelberger and Hornig at 792 cm^{-1} in HF in the samples prepared by direct condensation from the gas is a true librational mode and not a disorder-induced mode. It is also important to note that the peak in HF is found at a frequency of 1.38 times the frequency of the peak in DF which is the expected ratio of the square root of the reduced masses. As noted above the peaks identified as fundamental vibrations in this work in the librational region of HF and DF all obey such a harmonic mass dependence. In the Raman data reported here two modes, $L2$ and $L3$, are seen in the same region as the 792-cm^{-1} ir peak. Tentative assignments would then give the $L3$ mode B_1 symmetry since the pressure dependence of the $L3$ mode extrapolates to 776 cm^{-1} in HF and 564 cm^{-1} in DF at zero pressure which is closer to the frequencies of the mode seen by Kittelberger and Hornig[13] at 792 cm^{-1} in HF and at 572 cm^{-1} in DF. The $L2$ mode, which extrapolates to 722 cm^{-1} in HF and 515 cm^{-1} in DF at zero pressure, would have A_2 symmetry which is infrared inactive. The fourth librational mode expected would be the B_2 mode. Kittelberger and Hornig[13] show a peak at 962 cm^{-1} in HF and 699 cm^{-1} in DF. Anderson et al.[15] observed a peak at 943 cm^{-1} in HF and 696 cm^{-1} in DF. The ratio of the frequency of the HF peak to the DF peak for both studies is almost exactly 1.38, the square root of
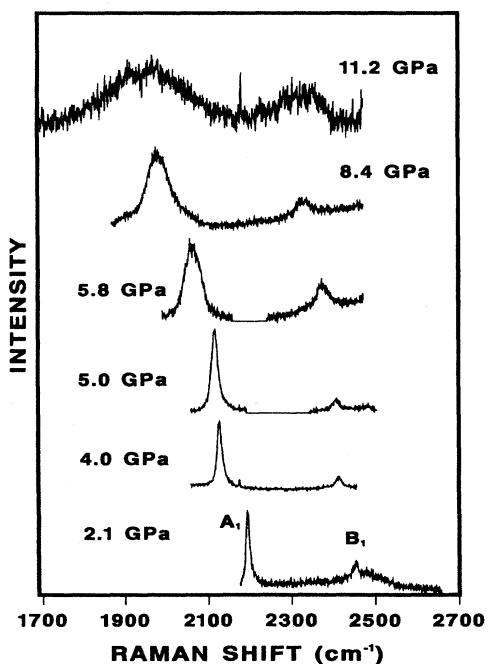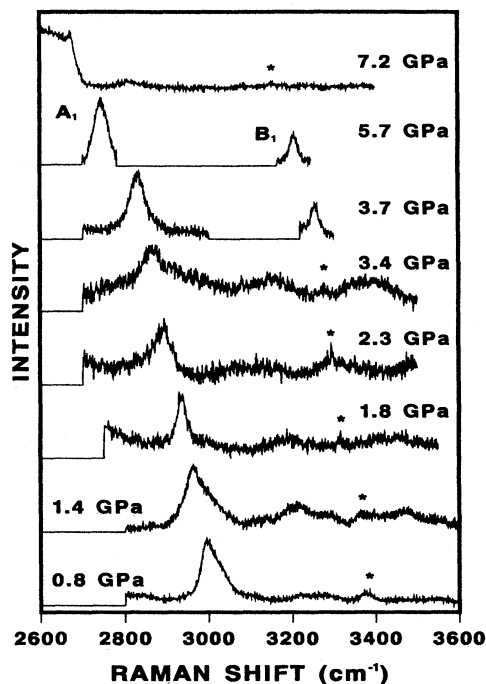

FIG. 9. Raman spectra of the A_1 and B_1 stretching modes in HF for a range of pressures. The B_1 mode is indicated by an asterisk in some of the spectra. The feature on the low-frequency end of the 7.2-GPa spectrum is part of the diamond second-order Raman spectrum.
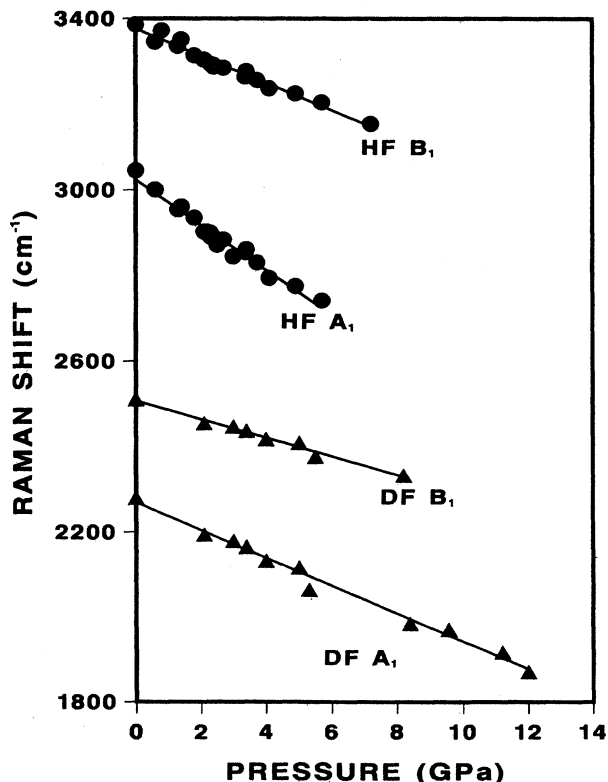

FIG. 8. Raman spectra of the A_1 and B_1 stretching modes in DF for a range of pressures.

FIG. 10. Pressure dependence of the A_1 and B_1 stretching-mode frequencies in HF and DF. The lines are linear regression fits.

the expected reduced mass ratio for harmonic oscillators. In some of our HF spectra there was a large broad feature in this region with no discernible pressure dependence. This feature could possibly be due to the diamond. In none of our spectra were we able to detect a feature that could be unambiguously identified as this fourth librational mode.

In summary, we make the assignment of the $L1$ mode as the A_1, mode, the $L2$ mode as the A_2 mode, the B_1 mode as the B_1 mode. The B_2 mode was not observed by us but we agree with the earlier assignments of this mode.

C. Stretching modes

In the stretching-mode region the A_1 symmetric and the B_1 antisymmetric modes were observed in both HF and DF. Stretching-mode spectra for a range of pressures for DF and HF are shown in Figs. 8 and 9, respectively. The strong combination bands of stretching modes with translational modes are especially evident in the HF spectra. The frequencies of the fundamental stretching modes decrease strongly with increasing pressure similar to other hydrogen-bonded systems. In the case of HF the scattered intensities of both stretching modes seem to significantly weaken at pressures above 5.7 GPa. Unfortunately at 7.2 GPa and higher, the A_1 mode shifts into the region of the diamond second-order Raman spectrum so that it was not possible to separate it from that background. The B_1 mode was very weak at 7 GPa and neither mode was seen above that pressure. As we have stated previously, both of these modes should disappear if the HF makes a transition into the symmetric D_{2h}^{17} structure. The modes in the stretching-mode region broadened significantly as the pressure increased, probably as a result of increasing pressure gradients. The pressure dependence of the A_1 and B_2 stretching modes in HF and DF in the C_{2v}^{12} structure is given in Fig. 10. These data were fit to straight-line functions of pressure which are given in Table II. The only disagreement with the earlier work in these data is that the HF mode frequencies do not extrapolate exactly back to the values obtained by Anderson et al. at zero pressure. This is interpreted as a small extra decrease in the stretching-mode frequencies at low pressure due to the initial softness of the HF crystal. The ratio between the HF and DF symmetric stretching-mode frequency is 1.33 at zero pressure and decreases to 1.29 at 10 GPa based on the fits to our data. This ratio would be expected to be 1.38 if the stretching modes were harmonic. The large deviation from the expected harmonic ratio suggests a large anharmonic effect which increases even further as the pressure increases. Use of an anharmonic double-well model to extract information from the data will be presented in Sec. IV.

IV. ANALYSIS

The analysis done here is largely based on the double-well-potential picture developed recently by Jansen et al.[20] We will use the pressure dependence of the A_1 stretching-mode frequencies in both HF and DF to ex-tract parameters relative to the potential well. It will be assumed that the potential well is identical for both HF and DF. The obvious effect of pressure is to cause a continual decrease in the frequency of these modes as a function of pressure. As shown above both the A_1 symmetric and the B_1 antisymmetric stretching modes decrease linearly in frequency with pressure. The analysis presented here will involve only the A_1 symmetric stretching mode of HF and DF. The potential for this mode will be symmetric about the midpoint of the coordinate between two fluorines. At low pressures, this potential has a barrier in the middle. As the pressure increases the barrier height will decrease strongly. At a critical pressure P^* the barrier will disappear. In a classical analysis this would be the pressure for the formation of the symmetric hydrogen bond although in a correct quantum-mechanical treatment the symmetric bond would form at somewhat lower pressure because of quantum considerations. As has been shown in Jansen et al.[19] this potential can be represented by the form

$$V(y) = \Phi_B (y^2 - b^2)^2 / b^4 , \qquad (1)$$

where Φ_B represents the height of the potential barrier above the minima and $\pm b$ represent the locations of the two equivalent minima of the potential. A sketch of this potential is shown in the inset in Fig. 11. The coordinate y is measured from the midpoint of the line connecting the two fluorines. The symmetric-stretching mode can be considered to be the motion of one hydrogen in one such well since all of the hydrogens move in phase. We shall see that at low pressures, the barrier height is of the order of 0.9 eV and the ground-state energy of the hydrogen stretch mode is of the order 0.2 eV. One can easily calculate the energies of the various vibrational quantum states in this well. Because of the barrier, all vibrational quantum states with energies less than the barrier height Φ_B will come in pairs corresponding to the tunnel splitting between the even- and odd-symmetry states. This splitting will be very small for the ground state and only slightly larger for the first excited state. In the spirit of Jansen et al. the difference between the two quantum states caused by tunneling will be considered as insignificant in the range of pressures in the present study where the barrier remains large compared to the zero-point motion. Thus the energy levels of these two states will be taken as the average of the energy levels of the corresponding tunnel-split states.

The goal of the present analysis is to determine the potential parameters from the experimental data. In order to easily calculate these parameters and compare with experiment, the vibrations of a hydrogen atom in one of these anharmonic wells will be examined using standard first- and second-order perturbation theory. We realize, of course, that perturbation theory will not be applicable as the barrier height becomes comparable to the vibrational frequency. Expanding the potential about the minima gives

$$V(x+b) = 4\Phi_B x^2 / b^2 + 4\Phi_B x^3 / b^3 + \Phi_B x^4 / b^4 , \qquad (2)$$

where x represents the displacement of the hydrogen

from the minimum located at b.

The harmonic frequency of the oscillator will then be given by

$$\omega = (8\Phi_B / b^2 \mu)^{1/2} ,$$ (3)

where μ is the reduced mass corresponding to the HF or DF molecule. The second-order perturbation for the cubic anharmonic term for the 0-1 transition will be $-\frac{15}{8}\hbar^2/b^2\mu$. The first-order perturbation for the 0-1 transition for the quartic anharmonic term will be $\frac{3}{8}\hbar^2/b^2\mu$. These terms can be combined to give a composite perturbation term of $-\frac{3}{2}\hbar^2/b^2\mu$. Note that the harmonic frequency is proportional to $(1/\mu)^{1/2}$ while the perturbation term is proportional to $1/\mu$. The resulting expression for the observed Raman frequency of the 0-1 transition is then,

$$\hbar\omega_{exp} = \hbar\omega_{har} - \Delta E_{pert}$$

$$= \hbar(8\Phi_B / \mu b^2)^{1/2} - (3\hbar^2 / 2\mu b^2) .$$ (4)

The difference in the mass dependence of these two terms makes it possible to extract the parameters of the model from the measurements of the symmetric-stretching frequencies in HF and DF.

As was noted in Sec. III, the ratio of the experimental symmetric-stretch mode frequencies is 1.33 at zero pressure and decreases to 1.30 at 6 GPa. A purely harmonic effect would give a ratio of 1.38. The decrease of this ra-
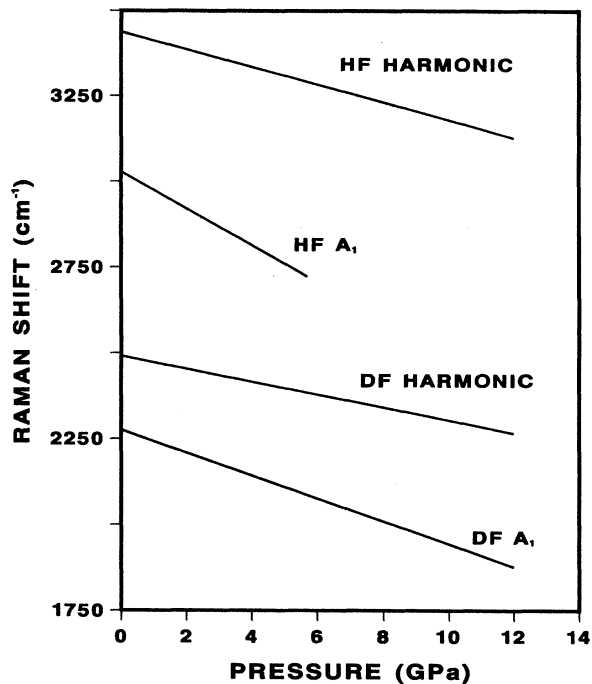

FIG. 12. The linear regression fits to the A_1 stretching-mode frequencies vs pressure for HF and DF from Fig. 10 along with the calculated *harmonic* frequencies for this mode. See text.
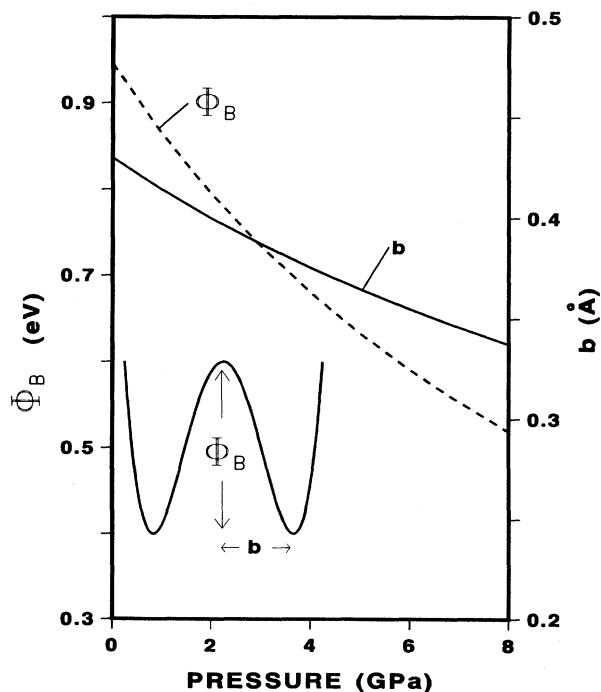

FIG. 11. The barrier height Φ_B (eV) and the position of the potential minima b (Å) as a function of pressure as determined using the perturbation analysis of the double-well-potential model and experimental A_1 frequencies. The inset shows the double-well potential. See text.
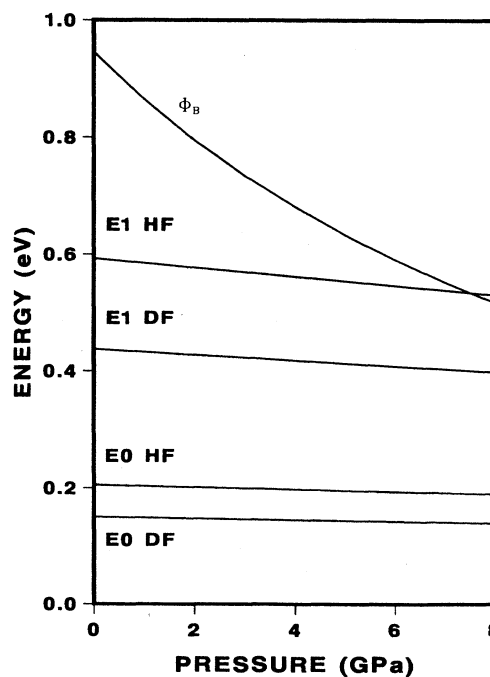

FIG. 13. Pressure dependence of the barrier height Φ_B along with the energies of the ground ($E0$) and the first excited state ($E1$) of the A_1 mode for HF and DF. See text.

tio tells us that anharmonic effects are becoming larger as the pressure increases which is in agreement with our simple notions of the barrier height strongly decreasing with increasing pressure.

We have analyzed the A_1 stretching-mode data for HF and DF using this procedure. The results of this analysis are shown in Figs. 11–13. The pressure dependence of the model parameters, Φ_B and b, as determined from this analysis are shown in Fig. 11. Figure 12 reproduces linear fits to the A_1 stretching-mode experimental data for both HF and DF which was presented in Fig. 10. Also shown are the pressure dependence of the harmonic frequencies for these modes as determined using the values of the parameters Φ_B and b given by the perturbation calculation. The anharmonic correction is the difference between the harmonic frequency and the experimental frequency. Since the experimental frequencies are linear functions of pressure, both the harmonic frequencies as well as the anharmonic correction are also linear in pressure. It is interesting to note that while the experimental frequencies for HF and DF extrapolate to zero frequency at pressures of 56 and 69 GPa, respectively, the harmonic frequencies for both HF and DF extrapolate to zero at the same pressure of about 100 GPa. The simple criterion in Jansen et al. would then put an expected transition where the potential barrier goes to zero at one-half of these pressures, which would then range from 28 GPa if one uses the experimental data for HF to 50 GPa if one uses the harmonic frequencies for either HF or DF. The harmonic frequencies have a ratio of 1.38:1 and the anharmonic corrections are in the ratio of 1.9:1 as required by the simple model that has been used.

Figure 13 shows the pressure dependence of the barrier height Φ_B along with energies of the ground and first excited vibrational states of the H atom in HF and the D atom in DF. We can see from this that both the ground and first excited-state energies are relatively insensitive to pressure while the barrier height decreases very rapidly with pressure. One notes that the barrier height crosses the energy of the first excited vibrational state for HF at about 7.5 GPa which is about where we see the disappearance of the stretching-mode Raman signal for HF as well as the other evidence for the symmetric hydrogen bond in HF. In contrast to this the barrier height will not cross the first excited state in DF until abut 13 GPa which is above the range of our measurements. One realizes that the exact results we obtain here are only suggestive of what is really happening because of the several approximations we have made. However, it is reassuring to see that the analysis of the pressure dependence of Raman data using isotopes can lead to the pressure dependence of potential parameters.

The perturbation analysis of the experimental data using the double-well model has given the pressure dependence of the model parameters. Using the model parameters we have been able to the calculate the A_1 stretching-mode energy levels of both HF and DF as a function of pressure. Qualitatively the results agree with the approach to hydrogen-bond symmetrization as seen in the experimental data.

V. SUMMARY

We have measured the Raman spectra of both HF and DF in the pressure range up 17 GPa at 25 K. In the translational-mode region we observed the A_1 mode in HF and both the A_1 and A_2 modes in DF. The A_1 translational mode shows very little isotope effect. Extrapolation of the pressure dependence of these modes agrees very well with the earlier studies on HF and DF.

In the librational region we have observed three of the four fundamental librational modes expected for the C_{2v}^{12} structure. These three librational modes, $L1$, $L2$, and $L3$, exhibit the reduced mass dependence expected for librational harmonic oscillators. The identification of these modes resolves some of the confusion in the earlier infrared and Raman studies done on HF and DF. We have made symmetry assignments of the librational modes which are in order of frequency $L1 = A_1$, $L2 = A_2$, $L3 = B_1$, and B_2 (which we were not able to see). There are a number of additional features in the HF librational spectra which we were not able to understand.

There was a dramatic change at about 6 GPa in the librational spectra in HF which also was accompanied by the disappearance of the translational and stretching modes. This change is consistent with a phase transition to the symmetric hydrogen-bonded phase of structure D_{2h}^{17}. No such transition was seen in DF up to pressures of 12 GPa. The quality of the spectra in HF is such as to make this only a suggested transition. The experiments need repetition in order to confirm this transition.

The stretching modes in HF and DF showed a strong decrease in frequency with increasing pressure as is characteristic of other hydrogen-bonded systems that have been studied. The symmetric-stretching modes in HF and DF are very anharmonic and become even more anharmonic as the pressure increases.

The experimental pressure dependence of the A_1 symmetric-stretching modes in DF and HF were used along with a perturbation procedure to obtain the pressure dependence of the parameters for the double-well model of Jansen et al. This analysis shows that the barrier height decreases strongly with pressure. It suggests that the energy of the first excited vibrational state for HF becomes equal to the barrier height at about 8 GPa which is comparable to the pressure where the evidence for the new phase in HF is seen.

The research presented here suggests that the study of strongly hydrogen-bonded materials under high pressure continues to be of interest and will lead to new insights in the field of hydrogen bonding.

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[1]S. A. Lee, D. A. Pinnick, S. M. Lindsay, and R. C. Hanson, Phys. Rev. B **34**, 2799 (1986).

[2]G. E. Walrafen, M. Abebe, F. A. Mauer, S. Block, G. J. Piermarini, and R. Munro, J. Chem. Phys. **77**, 2166 (1982).

[3]D. D. Klug and E. Whalley, J. Chem. Phys. **81**, 1220 (1984).

[4]K. R. Hirsch and W. B. Holzapfel, Phys. Lett. **101A**, 142 (1984).

[5]A. Polian and M. Grimsditch, Phys. Rev. Lett. **52**, 1312 (1984).

[6]M. Gauthier, Ph. Pruzan, J. C. Chervin, and J. M. Besson, Phys. Rev. B **37**, 2102 (1988).

[7]Allen I. Katz, Ph.D. dissertation, Arizona State University, 1987.

[8]P. G. Johannsen, W. Helle, and W. B. Holzapfel, J. Phys. C **8**, 199 (1984).

[9]M. Atoji and W. N. Lipscomb, Acta Crystallogr. **7**, 173 (1954).

[10]M. W. Johnson, E. Sandor, and E. Arzi, Acta Crystallogr. Sect. B **31**, 1998 (1975).

[11]P. A. Guigere and N. Zengin, Can. J. Chem. **36**, 1013 (1958).

[12]M. L. N. Sastri and D. F. Hornig, J. Chem. Phys. **39**, 3497 (1963).

[13]J. S. Kittelberger and D. F. Hornig, J. Chem. Phys. **46**, 3099 (1967).

[14]H. Boutin, G. J. Safford, and Velko Brajovic, J. Chem. Phys. **39**, 3135 (1963).

[15]A. Anderson, B. H. Torrie, and W. S. Tse, Chem. Phys. Lett. **70**, 300 (1980).

[16]A. Zunger, J. Chem. Phys. **63**, 1713 (1975).

[17]A. Karpfen and P. Schuster, Chem. Phys. Lett. **44**, 459 (1976).

[18]A. Karpfen, Chem. Phys. **47**, 401 (1979).

[19]A. Beyer and A. Karpfen, Chem. Phys. **64**, 343 (1981).

[20]R. W. Jansen, R. Bertoncini, D. A. Pinnick, A. I. Katz, R. C. Hanson, O. F. Sankey, and M. O'Keefe, Phys. Rev. B **35**, 9830 (1987).

[21]M. Springborg, Phys. Rev. Lett. **59**, 2287 (1987).

[22]R. Tubino and G. Zerbi, J. Chem. Phys. **51**, 4509 (1969).

[23]A. Axman, W. Biem, P. Borsch, F. Hossefeld, and H. Stiller, Discuss. Faraday Soc. **7**, 69 (1969).

[24]A. Anderson, B. H. Torrie, and W. S. Tse, J. Raman Spectrosc. **10**, 148 (1981).

[25]J. F. Higgs, W. Y. Zeng, and A. Anderson, Phys. Status Solidi B **133**, 475 (1986).

[26]L. Merrill and W. A. Bassett, Rev. Sci. Instrum. **45** 290 (1974).