

# Normal Mode Studies for Solids HF, HCl and Polyethylene According to the Pseudolattice Method

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Normal modes of solids HF, HCl and polyethylene having the exciting spectrometric phenomena have been evaluated by taking the lowest temperature phase of these species in the solid. The solids HF and HCl have the same space group as  $C_{2v}$  and polyethylene has a space group with  $D_{2h}$ . The normal modes were obtained by the valence force field with modified force constants and a quantitative description of the normal mode is adjusted by the potential energy distribution (PED). From the PED, the most fittable force constants are also obtained. We have intended to calculate the normal modes by using the smallest size of the model and the simple computational process. To remove the edge effects being occurred in constructing the single cluster model, different from the boundary condition being generally used up to now, the idea of pseudolattice method being successfully applied to MO calculations of solid was extended to normal mode analysis in order to give the same environment for all molecules in a chosen cluster. By using the above valence force field and boundary condition, we obtain the assigned frequencies and compare those results with the results obtained by others.

## Introduction

We test three polymeric materials having the exciting spectrometric phenomena<sup>1-6</sup>. The hydrogen fluoride was exhibited the large splitting between the internal modes, and it does not have the phase transition<sup>7</sup> with making the strongest hydrogen bond different from the other hydrogen halides. For the hydrogen chloride having planar zigzag hydrogen bond chains with three phase<sup>8-11</sup> in a solid, the contribution of the various electrostatic interactions are important for L<sub>0</sub>-T<sub>0</sub> splitting. The crystalline structures of HF and HCl are shown by X-ray diffraction studies and these crystals are built from infinite planar zigzag chains where each hydrogen halide is linked to the other hydrogen bond with space group  $C_{2h}^{12}$  ( $Bb2_1m$ )<sup>12,13</sup>. And polyethylene, consisting of infinitely long polymethylene chains and being observed the various sorts of splittings of the internal and lattice modes, was existed in three phases, such as orthorhombic<sup>14</sup>, monoclinic<sup>15</sup>, and high pressure form<sup>16</sup> in a solid. The orthorhombic polyethylene was the lowest temperature phase and its crystalline structure was understood as the all *trans*-planar chain with space group  $D_{2h}^{17}$  ( $P_{nma}$ )<sup>17</sup>. So far, many works were done on the normal vibrations<sup>2,18-22</sup> and spectra<sup>1,5,6,23-27</sup> of these species.

For choosing the model, no evidences for non-hydrogen bond pairs were found in hydrogen halide systems. These facts suggest that the interchain forces are much weaker than intrachain forces in hydrogen halide systems to say nothing of polyethylene. Those features suggest us that the single chain is sufficient to reproduce the normal modes, and the model is taken as one dimensional smallest zigzag cluster depicted in Figure 1. In treating these species theoretically, in order to remove the appeared end effect on constructing the model, as it were, so that atoms or molecules at the boundary are also felt the same environment being felt by atoms or molecules in a real solid, we apply the idea of pseudolattice method<sup>28,29</sup> to

the normal mode analysis. The conception of pseudolattice method is that the real crystalline solid can be represented by taking the smallest model with using the periodicity of molecules arranged regularly in a solid, where the pseudolattice method was successfully applied to MO calculations<sup>28,29</sup>.

A method for treating the normal vibrations of such an infinite chain having molecular repeating unit was proposed some years ago by Higgs<sup>30</sup>. Subsequently, others<sup>31-33</sup> have reformulated the method and applied it to polymer chain problems. To calculate the normal frequencies and normal coordinates, a computer program using the valence force field and having a very simple program input, was used and some details of the method are given in Ref. 34. In calculating the normal modes, a large splitting of internal modes of HF was obtained by inserting the interatomic interaction. Based on the calculations for HF, the Davydov splitting of HCl is also obtained, and the splittings of several bands for polyethylene are also obtained by combining the several interatomic interaction.

In this paper, we adjust the assigned frequencies obtained by the preceding procedure and predict the crystallographic assignment of each calculated frequencies. These results were compared with the results obtained by others and were listed in Table 1, 2, and 3.

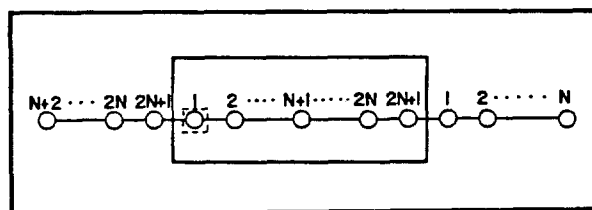


Figure 1. Central unit cell (rectangular frame) and the atoms outside it used to obtain periodic connections for four molecular units and the rectangle constructed by dashed line represents one molecular unit.

TABLE 1: Calculated Frequencies (in cm<sup>-1</sup>) of Solid HF

Our work	Others <sup>a</sup>	Experiment <sup>b</sup>	Assignment
3386	3404	3386	S(B <sub>1</sub> )
3044	3065	3044	S(A <sub>1</sub> )
937	552	943	L(B <sub>2</sub> )
738	1021	742	L(B <sub>1</sub> )
683	539	687	L(A <sub>2</sub> )
566	970	570	L(A <sub>1</sub> )
348	359	363	T(B <sub>1</sub> )
183	214	187	T(A <sub>1</sub> )
148	—	156	
66	—	57	T(A <sub>2</sub> )

<sup>a</sup> from Ref. 2; <sup>b</sup> from Ref. 23. where the notations S, L, and T indicate stretching, libration, and translation, respectively.

TABLE 2: Calculated Frequencies (in cm<sup>-1</sup>) of Solid HCl

Our work	Others <sup>a</sup>	Experiment <sup>b</sup>	Assignment
2749	2734	2749	S(B <sub>1</sub> )
2708	2728	2708	S(A <sub>1</sub> )
405	502	409	L(B <sub>1</sub> )
331	217	336	L(B <sub>2</sub> )
227	295	223	L(A <sub>1</sub> )
142	214	141	L(A <sub>2</sub> )
114	103	114	T(B <sub>1</sub> )
81	90	88	T(A <sub>1</sub> )
56	55	58	T(A <sub>2</sub> )

<sup>a</sup> from Ref. 39; <sup>b</sup> from Ref. 24 and 44. where the notations S, L, and T indicate stretching, libration, and translation, respectively.

## Theory

The following modified potential<sup>34-36</sup> suitable for both intra- and intermolecular motions is written as follows.

$$2V = K \sum_{ij} (\delta\gamma_{ij})^2 + H_\alpha \sum_{ijk} (\delta\alpha_{ijk})^2 + H_\tau \sum_{ijkl} (\delta\tau_{ijkl})^2 + \text{Interaction terms} \quad (1)$$

where  $K$ ,  $H_\alpha$ , and  $H_\tau$  are stretching, bending, and torsional force constant, respectively. The first term in eq. (1) represents the quadratic potentials between any two bonded atoms  $i$  and  $j$ . The next two terms describe the more commonly used angular deformation potentials;  $\delta\alpha_{ijk}$  is the change in a angle between the bonds  $ij$  and  $jk$ , and  $\delta\tau_{ijkl}$  is the change in a bondt torsion. And the last interaction terms are the crossterms describing the coupling between the above quadratic force fields, and these terms are obtained according to the objects by using the same procedure in Ref. 34.

The internal displacement coordinates,  $\delta\gamma_{ij}$ ,  $\delta\alpha_{ijk}$ , and etc. are expanded with Cartesian displacement as follows

$$\left(\frac{\partial\gamma_{ij}}{\partial x_s}\right)_0 = \frac{(x_i - x_j)_s}{\gamma_{ij}^0} = \begin{cases} \Phi_{s,ij} & \text{for atom } i \\ -\Phi_{s,ij} & \text{for atom } j \end{cases} \quad (2)$$

$$\left(\frac{\partial\alpha_{ijk}}{\partial x_s}\right)_0 = \left\{ \frac{\alpha_{ijk}(x_s^0 + 1/2\Delta) - \alpha_{ijk}(x_s^0 - 1/2\Delta)}{\Delta} \right\} = \Phi_{s,ijk} \quad (3)$$

The squares of the first derivatives constitute the force field matrix of the quadratic terms and the force field is represented as follows.

TABLE 3: Calculated Frequencies (in cm<sup>-1</sup>) of Polyethylene

Species	Our Work	Others <sup>a</sup>	Observed		Assignment
			Infrared <sup>b</sup>	Raman <sup>c</sup>	
A <sub>g</sub>	2879	2899	Inactive	2883	$\nu_s$ (CH <sub>2</sub> )
	2845	2845		2848	$\nu_s$ (CH <sub>2</sub> )
	1422	1437		1418	$\delta$ (CH <sub>2</sub> )
	1163	1164		1168	$\gamma$ (CH <sub>2</sub> )
	1135	1127		1131	Skeletal
	129	171		137	Rotational lattice mode
B <sub>1g</sub>	1375	1408	Inactive	1370	W (CH <sub>2</sub> )
	1302	1308		1295	t (CH <sub>2</sub> )
	1065	1051		1061	Skeletal
B <sub>2g</sub>	1372	1413	Inactive	1370	W (CH <sub>2</sub> )
	1299	1303		1295	t (CH <sub>2</sub> )
	1067	1051		1061	Skeletal
B <sub>3g</sub>	2887	2904	Inactive	2883	$\nu_s$ (CH <sub>2</sub> )
	2844	2838		2848	$\nu_s$ (CH <sub>2</sub> )
	1450	1455		1441	$\delta$ (CH <sub>2</sub> )
	1163	1164		1168	$\gamma$ (CH <sub>2</sub> )
	1133	1127		1131	Skeletal
	98	138		108	Rotational lattice mode
A <sub>u</sub>	1187	1184	Inactive	Inactive	W (CH <sub>2</sub> )
	1051	1055			t (CH <sub>2</sub> )
	52	59			Translational lattice mode
B <sub>1u</sub>	2922	2919	2919	nactive	$\nu_s$ (CH <sub>2</sub> )
	2855	2874	2851		$\nu_s$ (CH <sub>2</sub> )
	1470	1489	1473		$\delta$ (CH <sub>2</sub> )
	742	749	731		$\gamma$ (CH <sub>2</sub> )
	65	76	73		Translational lattice mode
	B <sub>2u</sub>	2923	2917	2919	Inactive
2855		2877	2851		$\nu_s$ (CH <sub>2</sub> )
1458		1479	1463		$\delta$ (CH <sub>2</sub> )
729		737	720		$\gamma$ (CH <sub>2</sub> )
97		105	109		Translational lattice mode
B <sub>3u</sub>	1182	1175	1175	Inactive	W (CH <sub>2</sub> )
	1053	1059	1050		t (CH <sub>2</sub> )

<sup>a</sup> from Ref. 53 and 54; <sup>b</sup> from Ref. 55 to 57; <sup>c</sup> from Ref. 58 to 60.

$$K \sum_{ij} (\delta\gamma_{ij})^2 = K \sum_{i,j} \sum_{s,t} \pm \Phi_{s,ij} \Phi_{t,ij} \delta x_s \delta x_t \quad (4)$$

$$H_\alpha \sum_{ijk} (\delta\alpha_{ijk})^2 = H_\alpha \sum_{i,j,k} \sum_{s,t} \Phi_{s,ijk} \Phi_{t,ijk} \delta x_s \delta x_t \quad (5)$$

Where  $s$  and  $t$  are the running index for Cartesian coordinates,  $x$  and  $\Delta$  are the Cartesian axis and infinitesimal, respectively, and  $\Phi_{ij}$  represent the element of directive cosine of the vector  $\gamma_{ij}$ . The explicit explanations and derivations are given in Ref. 34 to 36. Now, using the translational symmetry of molecules in a crystal or polymeric system (not a translational symmetry of unit cell), the molecules located at the boundary of the model are translated to the nearest position of the other boundary molecules. Since the matrix elements  $\Phi_{ij}$  are determined by the

$$D = b \cdot \begin{vmatrix} 0 & 1 & 2 & 1 \\ 1 & 0 & 1 & 2 \\ 2 & 1 & 0 & 1 \\ 1 & 2 & 1 & 0 \end{vmatrix} \quad E = \begin{vmatrix} 0 & 1 & 1 & 1 \\ -1 & 0 & 1 & 1 \\ -1 & -1 & 0 & 1 \\ 1 & -1 & -1 & 0 \end{vmatrix}$$

Figure 2. Interaction geometry matrices for one-dimensional chain of four molecular units with neighbour distance  $b$ .

position and mutual orientation of the atoms in the cluster, the geometrical periodicity that we have imposed on the interactions could be conveniently constructed by defining the interatomic distance matrix  $D$ , and the direction-cosine matrix  $E$  with respect to arbitrary direction of Cartesian axis. These matrices define the interaction geometry of a pseudomolecule consisting by four molecular units. They are built to be periodic and with symmetry properties of the investigated solid structure formed by translating the central Born-von Karman cell. The interatom distance matrix and its cosine matrix are useful to represent the pseudolattice method and depicted in Figure 2.

## Results and Discussion

(A) HF. There are two molecules in the primitive unit cell on  $C_2$  site<sup>13</sup> for HF with H—F bond distance of 1.02Å. From the correlation diagram, two H—F stretching modes with symmetric  $A_1$  and asymmetric  $B_1$  mode and seven lattice mode; three translations ( $A_1$ ,  $A_2$ , and  $B_1$ ) and four librations ( $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ ), are both infrared and Raman active except those of  $A_2$  species. A large separation between the symmetric mode ( $A_1$ ) and asymmetric mode ( $B_1$ ) in internal modes was explained in many aspects; due to the strongest hydrogen bond, electrostatic interactions<sup>20</sup> equivalent in HCl, and combinations of the stretching mode with the translational mode of  $A_1$ . A quantitative description of the normal modes is usually given in terms of the Jacobian matrix or potential energy distribution. Both these quantities have been determined together with the force field and the calculated frequencies.

In calculating the normal modes of HF system, we have chosen the simplest form of molecular force field, i.e.,  $K_1$ ; H—F stretching constant,  $K_2$ ; H···F hydrogen bond stretching constant,  $H_1$ ; F—H···F bending constant,  $\tau$ ; F—H···F—H torsional constant, and three interaction constants. The interaction constants;  $f_{kk}$  between the two stretching constant  $K_1$  and  $K_1$ ,  $f_{HH}$  between the two bending constant  $H_1$  and  $H_1$ , and  $f_{\kappa\tau}$  between the hydrogen bond stretching constant  $K_2$  and torsional constant  $\tau$ , were significant in all analyses. The initial choice of the force constants was based on Ref. 18. And then modified it to

TABLE 4: Valence Force Constants Used for Calculated Frequencies Listed in Table 1

Force constant	Coordinate involved	Values
$K_1$	H—F stretch	5.403 (mdyn/Å)
$K_2$	H···F hydrogen bond stretch	0.417 (mdyn/Å)
$H_1$	F—H F bend	0.282 (mdyn/Å/rad <sup>2</sup> )
$\tau$	F—H···F—H torsion	0.0085(mdyn/Å/rad <sup>2</sup> )
$f_{kk}$	F—H & F—H interaction	-1.172 (mdyn/Å)
$f_{HH}$	F—H···H & F—H···F interaction	0.0395(mdyn/Å/rad <sup>2</sup> )
$f_{\kappa}$	F—H···F—H & H···F interaction	0.007 (mdyn/rad)

adjust the frequencies. This set of trial force constants is given in Table 4.

The interaction constant  $f_{\kappa\kappa}$  clearly splits the internal mode into a symmetrical and an asymmetrical mode not affecting the other modes, as it were, this constant has increased the frequency of symmetrical mode and decreased the frequency of asymmetrical mode. Thus the more negative value of this constant gives the more splitting of internal modes. In librational motion, the interaction constant  $f_{HH}$  splits  $B_1$  mode and  $A_1$  mode, especially the interaction constant  $f_{\kappa\tau}$  splits  $B_1$  mode and  $B_2$  mode together with  $A_2$  mode, not effecting the other modes. These sets of interaction constants split the modes into the mode increasing the frequency and the mode decreasing the frequency, by the symmetry or the asymmetry of  $\sigma_v(xy)$  in  $C_{2v}$  space group. In translational mode, four normal modes were obtained but any interaction constant can not split these modes, different from librational mode. Although translational modes are slightly changed by the interaction constant, those are mainly effected by principal force constants which were represented as the total force constant except the interaction force constants. Especially, the  $B_1$  mode at 363  $\text{cm}^{-1}$  is not varied by any other force constant except the F—H···F bending constant in our calculations. In librational mode, out of plane motion ( $B_2$ ,  $A_2$ ) is observed near a higher frequency than in-plane motion, but in translational mode, in-plane mode ( $B_1$ ) is observed near a higher frequency than out of plane mode ( $A_1$ ). The lowest frequency of Raman peak not matched with infrared peak was known to  $A_2$  translational mode and it was explained with the tunneling mode<sup>37</sup> resulting from the motion of the proton between two minima of the potential within fluorine atoms. From the aspects of our results, this mode is shown that the motion of one molecule is perpendicularly translated to molecular axis and the other is co-linear. The translational mode observed at 156  $\text{cm}^{-1}$  was not known its origin in a present time. In our calculations, this mode was represented as the translational mode perpendicular to molecular axis, not a molecular propagation axis. The calculated results are compared with others and listed in Table 1.

(B) HCl. The molecular crystal<sup>9-11</sup>, HCl, has the structural transitions at 98.8°K and near 120°K, and chlorine atoms were existed in an orthorhombic structure with two molecules per primitive unit cell in this lowest temperature phase. From the spectroscopic activities<sup>24</sup>, seven optical modes of Raman active are infrared active except for two  $A_2$  species. The  $A_2$  and  $B_2$  species are out of plane vibrations while the  $A_1$  and  $B_1$  are in-plane. The exciting features of the observed spectra<sup>38,39</sup> are a large Davydov splitting<sup>4,40,41</sup> and a remarkable asymmetry of two exciton components. The high frequency tails observed in the infrared and Raman spectra have been interpreted by Savoie and Pezolet<sup>42</sup> as due to the L0-L0 splitting of the internal mode. Another interesting feature of the theoretical calculation is that the observed splitting was not reproduced by the short range atom-atom interactions<sup>3,39</sup> but reproduced only by the long range electrostatic interactions<sup>19</sup>, in spite of the various attempts to calculate the Davydov splitting by using the intermolecular force constants<sup>39,43,44</sup> or a model potential<sup>3</sup>.

In our calculations for HCl, the essential point is focused to

reproduce the Davydov splitting by using the intermolecular force constants. In calculating normal modes, we have chosen the simplest form of molecular force field, *i.e.*,  $K_1$ ; H—Cl stretching constant,  $K_2$ ; H···Cl hydrogen bond stretching constant,  $H_1$ ; Cl—H···Cl bending constant,  $K'$ ; Cl···Cl non-bonded stretching constant, and two interaction constants. The interaction constant  $f_{KK}$  between the two stretching constant  $K_1$  and  $K_1$ , was used to split the internal modes into a symmetrical and an asymmetrical mode. In facts, this interaction constant has influenced the internal mode, such as the positive effect on an asymmetric mode and the negative effect on a symmetric mode as increasing this interaction constant. The negative value of this constant increase the band gap between two internal modes up to corresponding to experimental splitting. Also the only dipole-dipole interaction among the various electrostatic interactions could not sufficiently explain the Davydov splitting, and when the value of this interaction constant was substituted for zero, the internal modes are not splitted as 2728.7 and 2728.5  $\text{cm}^{-1}$  in our calculations. Hence, this interaction constant is sufficient to obtain the Davydov splitting. In lattice modes, the interaction constant  $K_{HH}$  splits the upper two librational mode not effecting the other modes, thus the principal force constants are doing the important roles in adjusting the lattice frequencies. The results obtained by these procedures are compared with the others and listed in Table 2.

(C) *Polyethylene*. The crystal structure<sup>14-16</sup> and vibrational analysis<sup>5,6,21,22,27</sup> of polyethylene have been numerously studied by many workers, because of its familiarity and the exciting features such as the splittings of progression band in the vibrational spectra. A given vibrational mode of one molecule may be expected to split into two modes according to the phase relations, in-phase and out of phase, between the two molecular chains. By the correlation of the symmetry<sup>45</sup> between the molecule in the crystal lattice ( $D_{2h}$ ) and the isolated molecule ( $C_{2h}$ ), *i.e.*,  $A_g$  mode of  $C_{2h}$  is associated with  $A_g$  and  $B_{3g}$  mode of  $D_{2h}$ ,  $B_g$  mode with  $B_{1g}$  and  $B_{2g}$  mode,  $A_u$  mode with  $A_u$  and  $B_{3u}$  mode,  $B_u$  mode with  $B_{1u}$  and  $B_{2u}$  mode. The bands<sup>46</sup> showing the strong and perpendicular polarization observed at 2919, and 2851, around 1460, and 725  $\text{cm}^{-1}$ , are assigned to  $B_{1u}$  mode or  $B_{2u}$  mode, and the weak parallel band observed at 1176  $\text{cm}^{-1}$  is assigned to  $B_{3u}$  mode. In the crystal,  $B_{1u}$  and  $B_{2u}$  modes exhibiting the perpendicular polarization are polarized along the  $a$ -axis and the  $b$ -axis of the crystal, respectively. The correlation field splittings of  $\text{CH}_2$  rocking about 725  $\text{cm}^{-1}$  and of  $\text{CH}_2$  bending about 1460  $\text{cm}^{-1}$  are good examples of these cases. The  $B_{3u}$  mode being polarized parallel was splitted into  $B_{3u}$  mode, but experimentally no splitting is observed because of being  $A_u$  mode inactive in vibrational spectra. In the  $A_g$  and  $B_{2u}$  frequencies of  $\text{CH}_2$  bending mode<sup>27</sup>, the unusual frequency change with dependence on temperature may be explained partly by the Fermi resonance between the  $\text{CH}_2$  bending fundamentals and the overtone and/or combination of  $\text{CH}_2$  rocking modes<sup>45,46</sup>, and partly by some structural changes. Every normal mode of the single chain was splitted into two modes belonging to different symmetry species of the crystal, and the correlations among the molecular site<sup>3</sup> and space group are given in Ref. 46. The dipole-dipole interaction<sup>21</sup>, intermolecular potential<sup>22,49</sup>, and

*etc.*<sup>21,50</sup>, were used to explain these splittings, but we have tried to obtain these splittings by using the valence force field with the various interaction constants as the same procedures done in HF and HCl systems. The strength of the intermolecular interaction constants has direct effects on the vibrational frequencies of lattice modes or on the frequency gap of the correlation field splitting of the internal modes.

In calculating the normal modes of polyethylene, the C—H stretching constant effecting the stretching motion of hydrogen atom exerts influences only on the symmetrical and asymmetrical stretching, and the interaction constant  $f_{k_1k_1}$  between these two stretching constants splits the interval between the symmetrical and asymmetrical stretching frequencies. The lattice modes are mainly effected by three torsional constants and splitted by the interaction of these constants. In the other modes, as the assignment of mode may be differed by the direction in motion of hydrogen atom or carbon atom, the frequencies are varied by the bending or torsional constants containing the hydrogen atom and the various splittings are obtained by changing the interaction between these constants.

There are five lattice vibrations, *i.e.*, two rotational modes ( $A_g$  and  $B_{1g}$ ) being Raman active, two translational modes ( $B_{1u}$  and  $B_{2u}$ ) being infrared active, and another translational mode ( $A_u$ ) being inactive in both infrared and Raman spectra. The lattice mode frequencies are known as significantly effected by the temperature. The shift of translational mode ( $B_{1u}$ ) to the higher frequency as lowering the temperature, is explained by the contraction in the cell dimension<sup>51</sup> as decreasing the temperature. And the anharmonicities<sup>6,52</sup> have significant effects on the lattice modes, especially on  $A_g$  rotational mode.

For calculating the normal modes of polyethylene, we have taken seven principal constants and twelve interaction constants, where these constants and their values are listed in Table 6. To obtain the normal modes, it is inevitable to use many interaction constants for adjusting large experimental frequencies. By these reasons we unavoidably make use of the various interaction constants not orthogonal each other. So there appeared the mixing between  $\text{CH}_2$  bending modes and  $\text{CH}_2$  wagging modes, especially it is difficult to identify  $A_g$  mode and  $B_{3g}$  mode of  $\text{CH}_2$  bending. These modes are similar each other by mixing between  $\text{CH}_2$  bending and  $\text{CH}_2$  wagging except  $B_{3u}$  and  $B_{1g}$  mode of  $\text{CH}_2$  wagging. It can be easily identified between  $A_u$  mode and  $B_{1g}$  mode of  $\text{CH}_2$  wagging by introducing the interaction constant  $f_{k_2k_3}$ , and this constant splits the frequency between  $B_{1u}$  mode and  $B_{2u}$  mode of  $\text{CH}_2$  bending and the frequency between  $A_g$  mode and  $B_{3g}$  mode of  $\text{CH}_2$  bending. The frequencies

TABLE 5: Valence Force Constants Used for Calculated Frequencies Listed in Table 2

Force constant	Coordinate involved	Values
$K_1$	H—Cl stretch	4.063(mdyn/Å)
$K_2$	H···Cl hydrogen bond stretch	0.165(mdyn/Å)
$H_1$	Cl—H···Cl bend	0.127(mdyn/Å/rad <sup>2</sup> )
$K'$	Cl···Cl non-bonding stretch	0.045(mdyn/Å)
$f_{KK}$	Cl—H & Cl—H interaction	-0.125(mdyn/Å)
$f_{uu}$	Cl—H···Cl&H···Cl—H interaction	-0.015(mdyn/Å/rad <sup>2</sup> )

**TABLE 6: Valence Force Constants Used for Calculated Frequencies Listed in Table 3**

Force constant	Coordinate involved	Common atoms	Values
	Stretch (mdyn/Å)		
$K_1$	C—H		4.51
$K_2$	C—C		4.324
$K'$	H...H non-bonding		0.005
	Bend (mdynÅ/rad <sup>2</sup> )		
$H_1$	<CCC		1.027
$H_2$	<HCH		0.25
$H_3$	<CCH		0.9
	Torsion (mdynÅ/rad <sup>2</sup> )		
$t$	<CCCC		0.042
	Stretch-Stretch (mdyn/Å)		
$f_{K_1K_1}$	C—H & C—H	C	0.025
$f_{K_1K_2}$	C—C & C—H	C	0.045
$f_{K_2K_2}$	C—C & C=C	C	0.258
	Stretch-Bend (mdyn/rad)		
$f_{K_2H_1}$	C—C & <CCC	C—C	0.481
$f_{K_2H_3}$	C—C & <CCH	C—C	0.204
	Bend-Bend (mdynÅ/rad <sup>2</sup> )		
$f_{H_1H_3}$	<HCC & <HCC	C—H	0.22
$f_{H_2H_3}$	<HCC & <HCC	C—C ( <i>trans</i> )	-0.1
$f_{H_1H_2}$	<HCC & <CCC	C—C	-0.077
$f_{H_2H_3}$	<HCC & <HCC	C—C ( <i>gauche</i> )	0.1
$f_{H_3H_3}$	<HCC & <HCC	C ( <i>trans</i> )	0.05
$f_{H_3H_3}$	<HCC & <HCC	C ( <i>gauche</i> )	0.02
	Torsion-Torsion (mdynÅ/rad <sup>2</sup> )		
$f$	<CCCC & <CCCC	C—C	0.015

are varied with changing the mode by inserting the interaction constant  $f_{K_2K_3}$ , *i.e.*,  $B_{1g}$  mode of CH<sub>2</sub> wagging to  $B_{2g}$  mode of CH<sub>2</sub> wagging,  $B_{2u}$  mode of CH<sub>2</sub> bending to  $A_u$  mode of CH<sub>2</sub> wagging,  $B_{3g}$  mode of CH<sub>2</sub> bending to  $B_{1g}$  mode of CH<sub>2</sub> wagging,  $B_{3u}$  mode of CH<sub>2</sub> wagging to  $B_{3u}$  mode of CH<sub>2</sub> wagging,  $B_{1u}$  mode of CH<sub>2</sub> bending to  $B_{2u}$  mode of CH<sub>2</sub> bending,  $A_u$  mode of CH<sub>2</sub> wagging to  $B_{1u}$  mode of CH<sub>2</sub> bending,  $A_g$  mode of CH<sub>2</sub> bending to  $B_{3g}$  mode of CH<sub>2</sub> bending, and  $B_{2g}$  mode of CH<sub>2</sub> wagging to  $A_g$  mode of CH<sub>2</sub> bending. As this interaction constant owing to the interaction between C—C—H bending and C—C stretching within this bending exerts main influences on the skeletal motion of carbon atom, it is considered to effect sensitively on the mode of CH<sub>2</sub> bending and CH<sub>2</sub> wagging being alike in a skeletal motion and being not in accordance with the direction (along the Cartesian axis) of the motion of hydrogen atom. It is also conceived by the fact that  $B_{3u}$  mode of CH<sub>2</sub> wagging being co-linear for motions in hydrogen atoms and in carbon atoms is not influenced. Thus the interaction constant has direct influence on the normal modes to say nothing of vibrational frequencies. It was likewise occurred the mixing between CH<sub>2</sub> bending and CH<sub>2</sub> wagging by inserting the interaction constant  $f_{H_3H_3}$ , especially the more mixing is shown in three dimensional motions. This phenomena may be also explained by the fact that this interaction constant has the sensitive effect on the motion of hydrogen atoms. In our calculations, various features are obtained by introducing in-

teractin constants, such as, occurring the mixing between  $A_g$  and  $B_{2g}$  mode of skeletal modes by inserting the interaction constant  $f_{K_2H_1}$ , imposing the CH<sub>2</sub> wagging factor on  $B_{3g}$  and  $B_{2u}$  mode of CH<sub>2</sub> bending by inserting the interaction constant  $f_{H_3H_3}$ , and *etc.*, these force constants are listed in Table 6.

In ordinary normal mode analysis<sup>6,49,50,52</sup> and in our calculations, it has shown that lattice modes are slightly mixed with the internal modes in the same symmetry species, and such a mixing has an effect on lowering the lattice frequency. This feature may be considered as occurring by the reason of using the interaction constants being not orthogonal each other. If any force constant was not orthogonal to any other force constants among the total force constants, the normal modes can be mixed in a relatively weak mode. The same results may be also obtained by other normal mode calculations. The obtained values in our calculation are compared with others and listed in Table 3.

(D) *Effects due to the Boundary Conditions.* When the boundary condition of pseudolattice method is applied to normal mode analysis, it is more effective on the lower frequency region, and we also obtain the more mode, *i.e.*, the mode intensively trended toward out of plane libration for HF, the mode similar with  $B_2$  libration for HCl, and the mode similar with lattice modes for polyethylene. These modes are considered to appear due to the phase interaction between the adjacent phases. By enlarging the model, the dispersion curve may be obtainable. And when the infinite mass boundary condition is applied to HCl and polyethylene systems with 0.001 mdyn/Å of stretching constant between the boundary atom and the infinite mass, we obtain the interaction peaks at 10 cm<sup>-1</sup> and two at 8 cm<sup>-1</sup>, respectively. It is notable that out of plane motion is decreased as increasing this stretching constant, as it were, these modes are more align with the bond for a lower value of this constant but linear to the molecular axis at the higher. It may be thought for this feature that the motion along the propagation axis is increased by tightly binding the model and infinite mass as increasing this stretching constant. This stretching constant can vary this frequency upto 54 cm<sup>-1</sup> with 0.1 mdyn/Å for HCl and up to 53 and 69 cm<sup>-1</sup> with 0.5 mdyn/Å for polyethylene, then these frequencies are not influenced by this stretching constant. In polyethylene system, this constant give the influence on the lower frequencies too. Especially in HF system, the more interaction mode is not appeared under the infinite mass boundary condition merely increasing the lower frequencies, these frequencies are also increased until the value (0.8 mdyn/Å) being higher than other systems. These features can be explained as due to the strongest intermolecular and intramolecular bond. Using our boundary condition, limited maximum values in infinite mass boundary condition can be easily obtainable by changing the force constant set. The frequencies obtained with infinite mass boundary condition by using the same set of force constants, are smaller in its magnitude than the frequencies obtained by the pseudolattice method. These phenomena can be explained as there are some terms not considered in the infinite mass boundary condition, while the sufficient interactions are taken in the pseudolattice method. Both two boundary conditions only affect on the lattice modes, but not on the internal

modes.

## Conclusion

In our works, we obtain the various splittings of solids HF, HCl and polyethylene by using the set of interaction constants. The strength of the intermolecular interaction constant has directly affected on the vibrational frequency and on the frequency gap of the splitting, and especially on the normal mode.

By taking the smallest model according to the pseudolattice method, we save the computer times, and by taking the simple program input we easily deal with the normal coordinate analysis. As the pseudolattice method gives the same environment to all molecules in the model as in the real solid, the sufficient interactions are considered than under the infinite mass boundary condition and the good results are obtained.

Thus it is convinced for us that the pseudolattice method was also successfully extended to the normal coordinate analysis together with MO calculations of solids.

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