Intermolecular Potential, Vibrational Spectra, and Structures of Amino Acid Crystals. II. α-Glycine, L-Alanine, and DL-Alanine Crystals

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The lattice energies, the deviations of the structure parameters from the model equilibrium, the molecular distortions due to the intermolecular interaction and the vibrational frequencies of α-glycine, L-alanine and DL-alanine crystals were calculated from three sets of parameters for the pairwise atom-atom interaction potential functions. By comparing the calculated quantities with the observed ones, the combination of the exp-6 type non-bonded potential and the Lippincott type hydrogen bond stretching potential is shown to afford a better model of the intermolecular interaction in these crystals than the combination of the Lennard-Jones 6-12 potential and the general hydrogen bond 10-12 potential.

Evaluation of the intermolecular forces acting in amino acid crystals is an indispensable step for the conformational study of proteins. We have recently investigated the polarized Raman spectra of single crystals of glycine (α-form), L-alanine and DL-alanine,[1-4)] and have obtained a common set of potential parameters with which the observed vibrational frequencies of these amino acids can be elucidated fairly well. The intermolecular potential of amino acid crystal is very complicated, however, owing to the presence of many terms due to the exchange repulsion and dispersion force, the hydrogen bonding and the Coulomb interaction between atomic charges. Even the simplest description of these forces requires too many parameters to be estimated from the vibrational spectra alone.

The present work has been undertaken to check if the potential parameters used in our previous analyses of the vibrational spectra are compatible with the crystal structure itself. By taking account of the non-rigidity of the molecule as described in the preceding paper,[5)] the lattice energies, the equilibrium crystal structures, the molecular distortions due to the intermolecular force, the elastic constants and the vibrational frequencies have been calculated and a modification of a few potential parameters has been attempted. For the sake of comparison, the same calculations have been carried out by using the model potential proposed by Momany *et al.* on the basis of their extensive analyses of the conformations of amino acid crystals.[6)]

Calculation

The potential energy per molecule was written in the same functional form as those used in our previous analyses of the vibrational spectra of α-glycine, L-alanine, and DL-alanine crystals.[1-4)] The intramolecular part, V_{in}, is the simple Urey-Bradley type quadratic force field supplemented with the diagonal terms in the CO_2^- out-of-plane deformation coordinate and the internal rotation coordinates around the N–C and the C–C bonds.[7)] The intermolecular part, V_{ex}, is the sum of the pairwise potential terms of the three types,

$$V_1 = \frac{1}{2}\sum_i\sum_j [-A_{ij}r_{ij}^{-6}+B_{ij}\exp(-C_{ij}r_{ij})]$$

$$V_2 = -\frac{1}{2}\sum_i\sum_j D_{ij}\exp[-k_{ij}r_{ij}^e(r_{ij}-r_{ij}^e)^2/2D_{ij}r_{ij}]$$

and

$$V_3 = \frac{1}{2}\sum_i\sum_j e_ie_j\,\mathrm{erfc}(\sqrt{\pi}Kr_{ij})/r_{ij},$$

where r_{ij} is the distance between the atoms i and j, the index i runs over a single molecule and j over the others. The potential V_1 represents the exchange-repulsion and dispersion interaction for the atom pairs H···H, C···H, C···C, O···H(C), and N···O. V_2 is the Lippincott type stretching potential[8)] of the hydrogen bonds (N)H···O, and V_3 arises from the Coulomb interaction between the atomic charges e_i and e_j. The vector of the molecular distortion, $\boldsymbol{S}_{\text{in}}^c$, the correction vector for the lattice constants, $\Delta\boldsymbol{a}^*$, and that for the molecular translation and rotation, $\boldsymbol{T}_{\text{ex}}^*$, were calculated from Eqs. 9, 23, and 26, respectively, in the preceding paper,[5)] and V_{in} from

$$V_{\text{in}} = (1/2)\tilde{\boldsymbol{S}}_{\text{in}}^c\boldsymbol{F}\boldsymbol{S}_{\text{in}}^c,$$

where $\boldsymbol{F}$ is the potential energy matrix for the intramolecular vibrations. The lattice energy was then calculated from

$$V = V_{\text{in}} + V_{\text{ex}}.$$

An order-of-magnitude estimation of the zero point energy per molecule was made according to

$$V_0 = (1/2n)\sum_{i=1}^{6n-3}\nu_i^{\text{calcd}},$$

where n is the number of molecules per primitive unit cell and ν_i^{calcd} is the calculated value of the ith optical-active lattice frequency.

The calculation was carried out for two sets of potential parameters, Sets I and II. Both the sets consist of the same parameters as those used in our unified treatment of the vibrational spectra of α-glycine and DL-alanine crystals,[4)] except that the parameters A_{ij} and C_{ij} for the N···O contact in Set II were taken as 3266.1 kJ mol^{-1} Å^6 and 37.11 Å^{-1}, respectively. The meaning of this adjustment will be given in the next section. The summation limit for V_1 was taken to be 8 Å. The limit of 6 Å used previously is sufficient for the convergence of the vibrational frequencies, but causes truncation errors up to 10% for the lattice energy. According to Williams,[9)] the Coulomb potential V_3 was written in the form including the complementary error function as a convergence factor. In a preliminary survey of the Coulombic lattice sum, we recognized little indication of the convergence of V_3 on extending the summation limit to 40 Å in the absence of the convergence factor. When the convergence constant K was taken to be 0.20 and 0.05, however, the energy converged with enough accuracy at the summation limits of 20 Å and 40 Å, respectively. We calculated the complete Coulomb energies for several representative choices of K by Bertaut's method,[10] and estimated the errors due to the neglect of the reciprocal lattice sum to be about 4 kJ mol^{-1} for α-glycine and L-alanine crystals and about 13 kJ mol^{-1} for DL-alanine crystal. The comparatively large error for DL-alanine may be ascribed to the residual dipole moment of the unit cell resulting from the polar structure of this crystal.[11]

In order to compare the behaviors of various types of the model potential functions, the same calculations as described above were carried out for the model potential proposed by Momany *et al.* in their conformation analysis of amino acid crystals.[6] In these authors' model, which will be abbreviated as MCS model hereafter, V_1 is given by the Lennard-Jones 6—12 potential, V_2 by the general hydrogen bond 10—12 potential and V_3 is written in the form including the reciprocal of the effective dielectric constant in place of the convergence factor. All the potential parameters and the atomic charges were taken from the original works.[6]

In the calculation with Sets I and II, the atomic coordinates were taken from the neutron diffraction study for α-glycine crystal[12] and the X-ray analyses for L-alanine[13] and DL-alanine[11,14] crystals. The positions of the hydrogen atoms of alanine were then adjusted by scaling the bond vectors in such a way that the averages of the C–H and the N–H bond lengths in each crystal became equal to those in α-glycine crystal, 1.09 Å and 1.039 Å, respectively. The same coordinates were used in our previous analyses of the crystal vibrations.[1–4] The atomic coordinates for MCS model were calculated from those for Sets I and II in the following two steps. First we shortened the N–H bondlengths of glycine and alanine and the C–H bondlengths of glycine to 1.00 Å without changing the valence angles and the internal rotation angles relevant to these bonds. The lattice constants of α-glycine and L-alanine crystals were next changed from the experimental values to those reported to give the minimum energy of the model potential according to the calculation of Momany *et al.*[6] In this adjustment of the lattice constants, the fractional coordinates of the center of mass of each molecule along the crystal axes were kept unchanged from the experimental values. No adjustment of the lattice constants were made for DL-alanine crystal.

Results and Discussion

The calculated values of the lattice energies, the components of the correction vectors $\boldsymbol{T}^*_{\mathrm{ex}}$ and $\Delta\boldsymbol{a}^*$ and the diagonal elastic constants are listed in Tables 1 and 2 for the three sets of potential parameters investigated. The contributions of V_{in} and V_0 to the total energy are very small compared to those of V_{ex}, and may be disregarded at the present level of approximation. In support of the correctness of our

TABLE 1. LATTICE ENERGY, COMPONENTS OF Δa^* AND T^*_{ex}, AND DIAGONAL ELASTIC CONSTANTS OF α-GLYCINE CRYSTAL

	Set I		Set I′ [a]	Set II	MCS model[a]
R_{max}[b]/Å	40.0	20.0	40.0	40.0	20.0
K/Å^{-1}	0.05	0.20	0.05	0.05	0.00
V/kJ mol^{-1}	−222.4	−212.4	−203.6	−216.0	−100.3
V_{in}/kJ mol^{-1}	7.8	6.4	8.8	4.3	1.5
V_0/kJ mol^{-1}	3.4	3.4	3.1	4.0	3.5
Δa^*/Å	0.421	0.423	0.109	−0.005	−0.046
Δb^*/Å	0.860	0.930	0.091	0.076	0.065
Δc^*/Å	−0.251	−0.253	0.061	−0.167	0.018
$\Delta\beta^*$/radian	0.029	0.027	0.057	0.054	−0.019
T_1^*/Å	0.044	0.045	0.091	0.016	0.063
T_2^*/Å	0.504	0.494	0.031	0.145	−0.060
T_3^*/Å	−0.507	−0.497	0.007	−0.098	0.008
R_1^*/radian	−0.072	−0.068	0.009	−0.053	0.001
R_2^*/radian	0.063	0.064	0.099	0.076	−0.010
R_3^*/radian	−0.038	−0.036	−0.034	−0.018	0.043
C_{11}/kJ cm^{-3}	42.91	43.02	38.98	54.38	30.30
C_{22}/kJ cm^{-3}	22.71	21.74	22.65	32.88	27.25
C_{33}/kJ cm^{-3}	46.01	45.37	47.41	73.99	69.43
C_{44}/kJ cm^{-3}	7.16	7.16	6.17	7.88	−0.62
C_{55}/kJ cm^{-3}	9.18	8.95	9.35	12.61	11.56
C_{66}/kJ cm^{-3}	4.89	4.62	−13.73	10.61	8.79

a) Non-bifurcated hydrogen bond model. b) The summation limit for V_3.

TABLE 2. LATTICE ENERGY, COMPONENTS OF $\Delta \boldsymbol{a}^*$ AND $\boldsymbol{T}^*_{\mathrm{ex}}$, AND DIAGONAL ELASTIC CONSTANTS OF L-ALANINE AND DL-ALANINE CRYSTALS

	L-Alanine			DL-Alanine		
	Set I	Set II	MCS model	Set I	Set II	MCS model
V	−202.8	−194.4	−101.2	−200.5	−192.1	−50.1
V_{in}	11.8	9.3	2.8	7.3	5.7	5.0
V_0	3.3	3.7	3.0	3.2	3.5	3.9
Δa^*	−0.345	−0.267	0.255	0.654	−0.080	1.041
Δb^*	0.892	0.159	−0.076	−0.160	−0.074	−0.577
Δc^*	0.123	−0.029	0.025	−0.045	−0.131	−0.387
T_1^*	0.026	0.035	−0.026	−0.017	−0.013	−0.017
T_2^*	0.097	−0.064	−0.150	0.045	−0.141	−0.265
T_3^*	−0.095	−0.230	−0.060	−0.007	0.029	0.047
R_1^*	0.021	0.018	−0.003	−0.050	−0.018	−0.006
R_2^*	0.008	0.012	−0.039	−0.026	−0.042	−0.046
R_3^*	0.082	0.063	0.034	0.130	0.088	0.097
C_{11}	16.73	17.38	11.00	19.31	25.07	35.13
C_{22}	20.58	27.39	27.69	17.60	18.79	13.62
C_{33}	34.04	44.92	51.94	36.51	46.80	66.77
C_{44}	6.30	5.12	−0.17	10.14	10.24	7.22
C_{55}	6.90	6.48	3.53	11.59	10.84	6.93
C_{66}	6.57	5.24	2.89	6.83	6.05	3.21

The summation limit for V_3 is 40 Å for Sets I and II, and 20 Å for MCS model. K for Sets I and II is 0.05 Å^{-1}. The units are the same as those in Table 1.

algorithm, the lattice energies calculated for MCS model are comparable with those reported by the original authors.$^{6)}$ Recently, Gaffney *et al.* have estimated the heat of sublimation of glycine into the gaseous zwitterions by adding their mass-spectroscopic data of the heat of evaporation to the *ab initio* energy difference between the classical and the zwitterionic structures.$^{15)}$ The value of *ca.* 218 kJ mol^{-1} obtained by these authors agrees very well with the lattice energy calculated for both Sets I and II.

The components of $\Delta \boldsymbol{a}^*$ of DL-alanine crystal calculated for MCS model were large because we used the lattice constants not adapted to this model. As to the components of $\boldsymbol{T}^*_{\mathrm{ex}}$, MCS model seems to give an excellent result although these degrees of freedom have been left out of consideration by the original authors in determining the potential parameters.$^{6)}$ MCS model were found, however, to give negative values of the elastic constant C_{44} of α-glycine and L-alanine crystals, failing to keep these crystals stable against the shearing stress along the bc (bc* for α-glycine crystal) plane. In such a case, the correction vectors $\Delta \boldsymbol{a}^*$ and $\boldsymbol{T}^*_{\mathrm{ex}}$ indicate the direction of a pathway not toward a minimum but toward a saddle point on the potential supersurface. A large negative value of C_{66} was obtained for α-glycine crystal when the longest hydrogen bond, *i.e.*, one of the bifurcated hydrogen bonds with the bond distance 2.365 Å, was excluded from V_2 of Set I. This hydrogen bond is suggested accordingly to play an important role of stabilizing the crystal against the shearing stress along the ab plane. In a trial calculations without V_2 or V_3, some of C_{11}, C_{22} and C_{33} became negative, indicating that such a model cannot hold the crystal from expansion. The correction vector $\Delta \boldsymbol{a}^*$ of L-alanine calculated for MCS model has a fairly large component despite the use of the energy-minimizing lattice constants reported by Momany *et al.*$^{6)}$ A possible origin of such a discrepancy between these authors' calculation and the present result is the effect of the microscopic deformation which partly relaxes the macroscopic stress. A slight difference in the assumed molecular geometry or in the scheme of taking the lattice sum may also result in different equilibrium structures.

For each of the three amino acid crystals, the largest of Δa^*, Δb^*, and Δc^* calculated for Set I is positive in sign and is associated with the axis along the longest edge of the unit cell. Since about half of the hydrogen bonds per unit cell of each crystal are roughly directed along this axis, the largest deviation is attributable to deficiency of the potential parameters for the hydrogen bonds. Only worse results were obtained, however, in various trials to adjust the parameters in V_2 or to replace the Lippincott potential by the 10-12 potential. Accordingly, we tried to modify the exp-6 type potential in V_1 related to the N···O contact, for which the original parameters had been estimated from those for the N···N and the O···O contacts involving no hydrogen bonds.$^{16)}$ After the failure of several attempts to change the depth and the curvature of the potential curve, Set II was obtained by shifting the minimum to the same internuclear distance as that of the 10-12 potential used by Momany *et al.*$^{6)}$ The revision was readily carried out by expressing the potential in terms of the parameters ε, ρ, and μ introduced by Taddei *et al.*,$^{17)}$ and changing only ρ from 3.125 Å to 3.500 Å. As seen from Table 1, Set II was successful in confining all the elements

TABLE 3. DISTORTIONS OF SKELETAL DEFORMATION COORDINATES, δ[a] AND ρ,[b] AND INTERNAL ROTATION COORDINATES, t[c] (IN DEGREE)

		Theor.[d]	Set I[e]	Set II[e]	MCS model[e]
α-Glycine	δ(C′-C-N)	5.65	2.39	1.00	0.54
	δ(O-C′-O)	−6.25	−3.00	−2.61	−1.54
	ρ	2.33	1.75	0.41	0.62
	t(C-C′O_2)	19.15	7.86	−0.29	8.44
	t(C-NH_3)	−2.43	−3.57	−1.73	0.73
L-Alanine	δ(C′-C-N)	4.07	3.22	2.62	1.22
	δ(O-C′-O)	−6.10	−2.96	−2.63	−1.58
	ρ	3.23	2.13	2.25	0.63
	t(C-C′O_2)	−16.95	−11.49	−6.44	−5.10
	t(C-NH_3)	−0.74	−1.98	−1.25	−1.96
	t(C-CH_3)	−1.74	−13.91	−15.25	−7.19
DL-Alanine	δ(C′-C-N)	2.11	2.26	1.69	−1.07
	δ(O-C′-O)	−6.27	−2.04	−2.24	1.08
	ρ	6.22	1.97	2.03	1.14
	t(C-C′O_2)	−14.14	−10.13	−4.92	−2.09
	t(C-NH_3)	−0.73	−0.03	0.75	1.54
	t(C-CH_3)	−6.70	−3.67	−5.01	−6.33

a) The change of the valence angle shown in the parentheses. b) $\rho=(1/2)[\delta(\text{C-C}'\text{-O}_t)-\delta(\text{C-C}'\text{-O}_c)]$, where O_t and O_c are the oxygen atoms at the trans and the cis positions, respectively, of the nitrogen atom. c) The definition is given in Ref. 7. t(C-C′O_2) is zero when O_c is at the exact cis position of the nitrogen atom. t(C-NH_3) and t(C-CH_3) are zero for the staggered conformations. d) The experimental (X-ray or neutron diffraction) value minus the *ab initio* value. e) The lattice sums for V_3 were taken as in Table 2.

of $\Delta \boldsymbol{a}^*$ and $\boldsymbol{T}^*_{ex}$ within the range between −0.27 Å and 0.16 Å.

Table 3 shows the calculated distortions of the skeletal deformation and the internal rotation coordinates brought about by the balance between the internal and the external forces. The distortions of the stretching coordinates are all smaller than the uncertainty in the corresponding bondlengths reported in the literature on the X-ray analyses,[11–14] and are not given here. For the deformation coordinates, an alternative set of S°_{in} is available from the crystallographic data[11–14] by subtracting therefrom the theoretical values of the equilibrium structure parameters of the isolated zwitterionic glycine based on an *ab initio* LCMO-SCF method.[18] The signs of all the calculated distortions for Sets I and II agree with those predicted from the combination of the results of the crystallographic and the quantum-mechanical studies. As to the distortions of the internal rotation angles, all the signs calculated for Set I agree with those derived by assuming that the equilibrium structure of the isolated zwitterionic amino acids takes the staggered conformation around the N–C and the (CH_3)–C bonds and the planar conformation around the C–(CO_2) bond. Set II gave the wrong sign to the distortion of the internal rotation angle of the CO_2 group of α-glycine crystal, while MCS model predicted the sign of this distortion of the three amino acids correctly. At present, accuracy of this sort of calculation seems to be far from sufficient for discussing the difference in the molecular structure between L-alanine and DL-alanine crystals.

An iterative search for the minimum of the model potential according to the Newton-Raphson method[19] was carried out by taking the summation limit and the convergence constant for V_3 as 20 Å and 0.20, respectively. This limit was not large enough to disregard the effect of the neglected reciprocal sum, but was chosen in order to save computing time. Whenever the energy did not decrease in a single step, the correction vectors $\Delta \boldsymbol{a}^*$ and $\boldsymbol{T}^*_{ex}$ were multiplied by a damping factor 0.5. The iteration was repeated until all the elements of $\Delta \boldsymbol{a}^*$ and $\boldsymbol{T}^*_{ex}$ became less than 0.001 Å for the length and 0.001 radian for the angle. Set I failed to give any convergence of this procedure for L-alanine, leading to destruction of the crystal with negative infinite energy. Diverging results were obtained for the three amino acid crystals also by using MCS model. The success of this model for α-glycine and L-alanine crystals reported by Momany *et al.*[6] may be ascribed accordingly to the fixing of some degrees of freedom of molecular motions. The calculated equilibrium structures for the converging cases are described in Table 4 in terms of the lattice constants, the coordinates of the centers of masses and the Eulerian angles which define the principal axes of inertia of the molecules with reference to the unit cell axes. The maximum and the average distances between the calculated and the experimental atomic positions are also shown for the sake of comparison. Although the Eulerian angles seem to indicate that the calculated and the experimental orientations of the molecules are quite different from each other, the average deviations of the atomic positions are not too large, expecially for Set II, in comparison with the thermal motions of atoms in usual crystals. It is worth noting that these structures satisfy the equilibrium condition for all the degrees of freedom

TABLE 4. EXPERIMENTAL AND CALCULATED STRUCTURE PARAMETERS[a] AT EQUILIBRIUM

		α-Glycine			L-Alanine		DL-Alanine		
		Obsd	Set I	Set II	Obsd	Set II	Obsd	Set I	Set II
Lattice constants	a/Å	5.105	5.014	5.120	6.032	6.368	12.060	11.574	12.133
	b/Å	11.969	11.991	12.036	12.343	12.127	6.05	6.496	6.204
	c/Å	5.465	5.384	5.569	5.784	5.816	5.82	5.564	5.829
	β/°	111.70	108.65	109.22					
Coordinates of centers of masses	x_g/Å	0.679	0.806	0.769	3.184	3.331	1.621	1.591	1.636
	y_g/Å	1.411	1.299	1.357	1.641	1.642	1.662	1.875	1.619
	z_g/Å	−0.090	−0.060	−0.056	2.702	2.575	1.700	1.627	1.703
Eulerian angles[b]	ϕ/°	8.64	2.62	3.16	31.05	36.33	115.42	144.92	124.77
	θ/°	48.39	47.99	46.40	10.95	9.91	11.96	10.19	11.67
	χ/°	77.64	72.17	73.58	52.57	44.37	120.08	156.84	134.17
Δr/Å[c]	average		0.176	0.132		0.224		0.355	0.127
	max.		0.259	0.218		0.286		0.574	0.204

a) The experimental structures are taken from Refs. 11—13. b) The Eulerian angles are defined according to Ref. 20 with the convention that $I_1 > I_2 > I_3$. c) The distance between the experimental and the calculated atomic positions.

TABLE 5. CO_2 TORSIONAL FREQUENCIES AND LATTICE FREQUENCIES/cm^{-1}

α-Glycine				L-Alanine				DL-Alanine			
Obsd	I	II	MCS	Obsd	I	II	MCS	Obsd	I	II	MCS
	a_g				a				a_1		
194	*194*	*202*	229	190	*190*	219	277	180	*181*	205	262
178	170	184	*177*		160	*185*	*200*	145	141	*170*	193
155	136	164	145	137	130	145	145	115	121	136	*183*
	117	143	119	112	107	129	127	102	93	122	137
109	104	118	95	103	87	84	85		89	79	56
74	74	73	55	47	49	42	34		47	40	21
51	44	68	34		45	37	0		b_1		
	a_u				b_1				*180*	*211*	253
226	*217*	*218*	231	192	*184*	206	*245*	150	137	164	*191*
	139	185	*188*	157	158	*176*	*193*	122	125	141	180
	130	149	146	138	129	151	171	117	111	107	111
	87	122	69	112	102	119	130	90	84	93	89
	66	68	57	103	87	114	106	72	78	77	51
	43	43	10		83	86	91		a_2		
	b_g				b_2			180	*176*	204	248
	208	*210*	230		*193*	*224*	252	160	160	*171*	191
178	166	180	*191*	144	137	162	*181*	145	119	148	*173*
163	134	167	146	112	123	143	137	115	98	111	154
109	122	136	117	86	99	104	117	98	88	105	116
84	99	114	96	73	80	80	80	90	81	84	81
74	83	101	68	48	76	74	65		74	70	54
51	60	75	27		b_3				b_2		
	b_u			190	*199*	*224*	*247*		*190*	*214*	*251*
	210	*225*	230	137	140	169	194	150	136	171	231
175	170	185	*164*	128	130	143	162	115	115	122	143
140	140	167	133	103	112	124	126	98	98	106	105
91	112	137	114	98	105	99	93	90	80	77	74
	83	96	95	47	83	79	64	72	79	74	63

The calculated frequencies to which the CO_2 torsional mode contributes dominantly are shown in italics.

of atomic motions under the influence of the internal and the external forces of the model. The numbers of iterations required to reach the energy minimum were 9 to 10 for Set I and 6 to 7 for Set II, being even smaller than the number of the adjustable parameters in the latter case.

The deviation of the calculated lattice constants from the observed values in Table 4 differs considerably from the initial guess of the corresponding elements of $\Delta\boldsymbol{a}^*$ in Tables 1 and 2. The inversion of signs is encountered in many cases and the structure of α-glycine crystal can be predicted by Sets I and II equally well after the iteration. Such discrepancies between the initial guess and the final result are attributable to the higher-order elastic constants as well as to the correlation between $\Delta\boldsymbol{a}^*$ and $\boldsymbol{T}^*_{ex}$, both neglected in the present treatment.

The calculated and the observed frequencies of the lattice vibrational modes and the CO_2 torsional mode are shown in Table 5. In each symmetry species of the three amino acid crystals, the CO_2 torsional mode is the lowest-frequency internal mode and apts to couple appreciably with the lattice modes. Among the three sets of the potential parameters, Set I gave the closest fit between the calculated and the observed frequencies, and Set II ranks next. There are systematic deviations of the calculated frequencies for Sets I and II toward the lower- and the higher-frequency sides, respectively, of the observed values. For about half the data in Table 5, the observed frequency falls between the corresponding frequencies calculated from these two sets. On the other hand, MCS model failed to reproduce the observed frequencies between 200 and 140 cm^{-1} of L-alanine and DL-alanine crystals, and led to a vanishing frequency in the totally symmetric species of L-alanine. As to the factor group splittings of the deformation modes of the alkyl groups, the results for Sets I and II are essentially the same as those reported previously.[1–3] Compared to these sets, MCS model gave too large splittings of about 30 cm^{-1} for the CH_3 asymmetric deformation mode of DL-alanine crystal, and too small splittings of about 3 cm^{-1} for the CH_2 bending mode of α-glycine crystal. This result seems to reflect the difference in the dependence of $\partial^2 V/\partial^2 r$ on r between the 6-12 and the exp-6 potentials for the H···H contact. By substituting the potential parameters used in this work, we have confirmed that the former falls off more rapidly than the latter in the range between 2.3 and 3.0 Å in which the nearest-neighbor H···H distances of the alkyl groups of α-glycine, L-alanine and DL-alanine crystals are included.

According to the present calculation, the combination of the exp-6 type non-bonded atom-atom interaction potential and the Lippincott type hydrogen bond stretching potential gives more reasonable results with respect to the lattice energy, the crystal structure and the vibrational frequencies of the three amino acid crystals, than the combination of the Lennard-Jones 6-12 type and the 10-12 type general hydrogen bond potential. There is no assurance, however, as to whether the Lippincott potential is the best representation of the hydrogen bond stretching of amino acids in general. Furthermore, our choice of the parameter r^{e}_{ij}., which is the intrinsic equilibrium distance of the hydrogen bond, in V_2 (2.0 Å)[4] is very different from the original value of Lippincott and Schroeder (0.97 Å),[8b] and is rather similar to the equilibrium distance of the 10-12 general hydrogen bond potential given by Momany *et al.*[6] Further studies on the other amino acid crystals should be carried out extensively in order to settle this controversy.

The numerical calculations were carried out on a FACOM M200 computer at the Data Processing Center of Kyoto University.

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