BULLETIN OF THE
KOREAN CHEMICAL SOCIETY

Lattice Vibrational Calculation of Orthorhombic Hydrogen Chloride

Kyoung Tai No

Department of Chemistry, Soong Jun University, Seoul 151, Korea

Mu Shik Jhon

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150, Cheong Ryang Ri, Seoul 131, Korea (Received November 26, 1984)

The lattice vibrational calculation of orthorhombic hydrogen chloride is performed using physically realistic potential function which can reproduce the X-ray structure and heat of sublimation of the low temperature phase. The polar coordinates representation is introduced in order to describe the intermolecular interactions in a molecular crystal. The splitting in internal modes is calculated as 49 cm^{-1} and the other modes are in good agreement with experimental results.

Introduction

Molecular crystals are good subjects for the investigation of intermolecular interactions. The solid hydrogen chloride, the molecular crystal, has a first order phase transition at 98.4 K and the low temperature phase has face centered orthorhombic structure with space group $C_{2v}^{12}(Bb2_1m)$.[1,2] Primitive unit cell contains two molecules on C_s symmetry sites. Although many theoretical[3-9] and experimental[10-14] investigations are made on this orthorhombic crystal, its lattice vibrational and electronic structures are far from being completely understood. Especially, in the lattice vibrational study, many models are proposed in order to explain vibrational frequencies and absorption intensities of lattice modes. Many experimental workers assigned the librational modes to the spectroscopically observed data but their assignments are not consistant.

The purpose of this work is to propose physically realistic potential functions and to describe any degree of freedoms of molecular motions in a molecular crystal, and to calculate the lattice vibrational frequencies and modes.

Calculation

(a) *Potential Functions.* In this calculation, three kinds of intermolecular potential functions are used. For short range interaction, Lennard-Jones(L-J) 6-12 potential functions are introduced. Coulomb and polarization interactions are used for the long range interaction. For the electrostatic and dispersion-repulsion potentials, atom–atom pair interactions are used in order to remove the equilibrium difficulties in obtaining the minimum points in potential energy surface.

$$\phi_{el}(\gamma_{ij}) = q_i q_j / \gamma_{ij} \tag{1}$$

$$\phi_{d-r}(\gamma_{ij}) = 4 \varepsilon \varepsilon_{ij} \left[(\sigma_{ij}/\gamma_{ij})^{12} - (\sigma_{ij}/\gamma_{ij})^{6} \right] \tag{2}$$

$$\phi_{pol}(\gamma_{ij}) = -\frac{1}{2} \vec{\varepsilon}_b(\gamma_c) \hat{\alpha} \vec{\varepsilon}_b(\gamma_c), \tag{3}$$

where r_{ij} is a interatomic separation, and q_i and q_j are the net atomic charges on the i-th and j-th atoms, $|q_i| = |q_j|$. The magnitude of q is obtained from observed dipole moment of gas phase HCl molecules[15], ε_{ij} and σ_{ij} are the L-J potential parameters. As shown in Figure 1, nearest interatomic distance between Cl-Cl in ab plane is shorter than any other Cl-Cl distances and this is the evidence for strong interactions between HCl molecules along the b-axis. With spherically symmetric dispersion-repulsion potential function, this quantum mechanical phenomena can not be explained and can not reproduce the lattice parameters of X-ray diffraction studies. In order to obtain the observed lattice parameters at the minimum point in the calculated potential energy surface, two sets of L-J potential parameters are used for each Cl-Cl and H-Cl atom pairs. For the description of nearest Cl-Cl and H-Cl interactions in ab plane, $(\varepsilon_{ClCl_1}, \sigma_{ClCl_1})$ and $(\varepsilon_{HCl_1}, \sigma_{HCl_1})$ are used, respectively, and for the other Cl-Cl and H-Cl atom pairs, $(\varepsilon_{ClCl_2}, \sigma_{ClCl_2})$ and
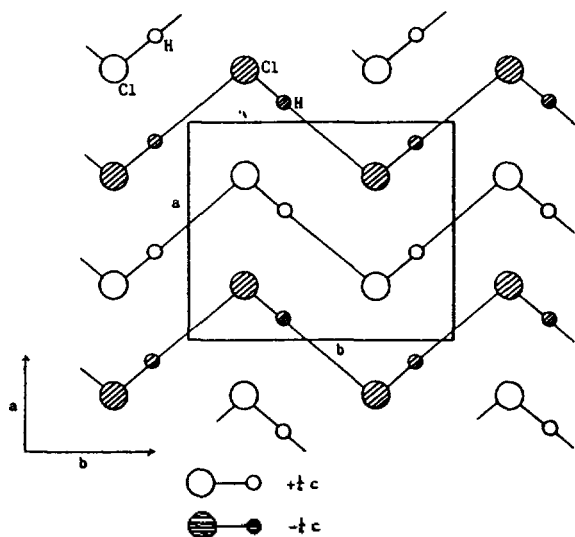
Figure 1. Crystal structure of face centered orthorhombic HCl. At 92.4 K, a = 5.082, b = 5.410, and c = 5.826(A), for face centered orthorhombic hydrogen chloride.

(ε_{HCl_2}, σ_{HCl_2}) are used, respectively. In polarization interaction, $\hat{\alpha}$ (α_ϕ, $\alpha_{\perp 1}$, $\alpha_{\perp 2}$) is a polarizability tensor[16] and $\bar{\varepsilon}_b(r_c)$, (ε_ϕ, $\varepsilon_{\perp 1}$, $\varepsilon_{\perp 2}$), is the electric field at the polarization center (0.1 × d_{HCl} from the center of Cl atom) of HCl molecule. The lattice sums include all the molecules within 25Å from one arbitrary molecule and this include more than 99 % compared with the extrapolated value. For dispersion–repulsion interaction, the molecules within 10Å from a central molecule are considered in the calculation.

(b) *Determination of L–J Potential Parameters.* The potential energy (ϕ_c) of the lattice used in this calculation is defined as follows;

$$\phi_c = \frac{1}{2} \{ \sum_{\substack{i = \text{all the surrounding} \\ \text{molecules}}} \sum_{\substack{J = H, Cl \text{ atoms of one} \\ \text{arbitrary molecule}}} \phi_{el} (\gamma_{ij}^\circ) + \phi_{d-r} (\gamma_{ij}^\circ) \} + \phi_{pol} (\gamma_c) \tag{4}$$

where r_{ij}° is the equilibrium distance at 0 K. The crystal lattice energy at absolute zero is expressed as

$$\Delta H_s^\circ = \phi_0 + E_z \tag{5}$$

where ΔH_s° is the enthalpy of sublimation at 0 K and E_z is a zero point energy. ΔH_s° is -4.803 kcal/mole[17] and E_z is 0.285 kcal/mole (calculated from Debye temperature, $E_z = 9/8NK_D$). From equation (5), potential energy of the HCl lattice is -5.088 kcal/mole. Six L–J parameters (ε_{ClCl_1}, σ_{ClCl_1}, ε_{ClCl_2}, σ_{ClCl_2}, ε_{HCl_1}, σ_{HCl_1}) are determined using constraints. ε_{HCl_2}, σ_{HCl_2}, ε_{HH}, and σ_{HH} are obtained from experimental data ($\varepsilon_{HCl_2} = (\varepsilon_{ClCl_2}\varepsilon_{HH})^{1/2}$ and $\sigma_{HCl_2} = (\sigma_{ClCl_2}\sigma_{HH})^{1/2}$).

(i) Constraint of lattice parameter

$$\sum_{i=1}^{n} \{ (\frac{\partial \phi \text{ (cal)}}{\partial X_i}) X_{i(eq)} \}^2 = A \tag{6}$$

(ii) Constraint of potential energy of the HCl crystal

$$\{ \phi_c - \phi \text{ (cal)} \}^2 = B$$

where $n(=6)$ is the number of lattice parameters (a, b, c, d_{HCl}, θ, ψ) and X_i is the lattice parameters, and X_i (eq) is the equilibrium lattice parameters. In the determination of L–J parameters, the function $A + bB$ is used as optimized function, especially in this

TABLE 1: Optimized Lennard–Jones Parameters

	ε (kcal/mole)	σ (A)
Cl–Cl[a]	0.6037	3.465
Cl–Cl[b]	0.5002	3.594
H–Cl[c]	0.3522	2.016
H–Cl[d]	0.2264	2.619
H–H	0.0726	2.138

[a]Chlorine–chlorine atom pair in ab plane (ε_{ClCl_1}, σ_{ClCl_1}). [b]The other chlorine–chlorine atom pairs (ε_{ClCl_2}, σ_{ClCl_2}). [c]Hydrogen–chlorine atom pairs along the b-axis(ε_{HCl_1}, σ_{HCl_1}). [d]Obtaind from geometric means, $\varepsilon_{HCl_2} = (\varepsilon_{ClCl_2}\varepsilon_{HH})^{1/2}$, $\sigma_{HCl_2} = (\sigma_{ClCl_2}\sigma_{HH})^{1/2}$. [e]Obtained from van der Waals radius of hydrogen atom.
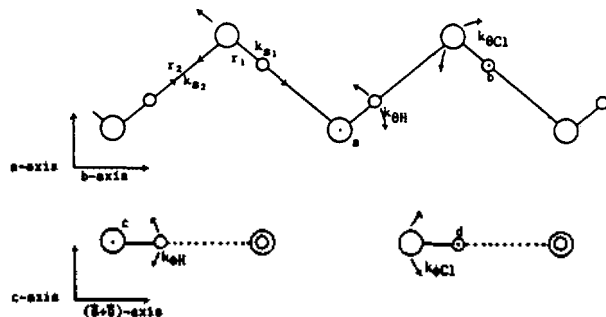

Figure 2. Polar coordinates used in this calculation. The polar coordinates θ_H, θ_{Cl}, ψ_H and ψ_{Cl} have their origin at a, b, c, and d, respectively. Stretching coordinates S1 and S2 are correspond to polar coordinates r1 and r2 when θ_H, θ_{Cl}, ψ_H, and ψ_{Cl} are fixed.

calculation $b = 1$. In Table 1, optimized potential parameters, which are reasonable values for the orthorhombic HCl crystal, ate listed.

(c) *Polar Coordinates and Force Constants.* In molecular crystals, clear distinction can be made between intermolecular and intramolecular motions. Internal coordinates are suitable for the representation of intramolecular motions because most of molecules in molecular crystals are the covalent bonding molecules. For the intermolecular motion, especially for the restricted translational and rotational motions, the internal coordinates representation is unrealistic. Because the intermolecular interactions in the molecular crystal, are multicentered, the bond axis between interacting molecules are not clearly defined. Therefore the representations of bending and torsional motions containing intermolecular interaction axis are physically unrealistic.

In this calculation, polar coordinates (q_i) representations are used and six force constants are assigned to these coordinates per one HCl molecule. Two of them are stretching force constants (k_{s1}, k_{s2}) corresponding to the r1 and r2 coordinates, respectively. The polar coordinates are described in Figure 2. Force constants are obtained using harmonic oscillator approximation as follows;

$$k_{q_i} = \frac{2\Delta \phi_i \text{ (cal)}}{\Delta q_i^2} \tag{8}$$

where Δq_i, is a small displacement of ith coordinate and k_{q_i} is a force constant correspond to the coordinate q_i. $\Delta \phi_i$(cal) is defined as;

$$\Delta \phi_i \text{(cal)} = \phi (q_1^\circ, q_2^\circ, \cdots) - \phi (q_1^\circ, q_2^\circ, \cdots q_i^\circ \pm \Delta q_i, \cdots) \tag{9}$$

where q_i^0 is an equilibrium position. In our calculation, Δq_i is 0.001Å for k_{r1} and k_{r2}, and 0.001 radian for angle displacements.

Force constants are listed in Table 2. In the lattice vibrational calculation, mass-weighted cartesian coordinate method[18] is used.

Results and Discussions

In Table 3, the calculated frequencies and assignments of the normal modes are listed and compared with the other calculations and experimenal results. The mode assignment of each frequency is made using the eigenvectors in a dynamical matrix and the lattice vibrational modes described by Ito, et al.[3] Most interesting result in Table 3 is the splitting of internal modes (B1, A1), 49 cm⁻¹. There have been various attempts to calculate the splitting ($\Delta \nu_{int}$), and good results are obtained by Ghosh[8], Schettino and Salvi[9]. But none of the models explain both this splitting in internal modes and the other external vibratinal modes, simultaneously.

From the view point of intermolecular potentials in HCl crystal, two factors mainly contribute to the splitting of the internal modes. One is the influence of H-bond along b-axis and

TABLE 2: Force Constant Corresponding to the Polar Coordinates Described in Figure 2

	equilibrium position[a]	force constants (mdyne/A)
k_{s1}	1.25048(A)	4.15[b]
k_{s2}	2.461(A)	0.165
$k_{\theta H}$	0.057(rad)[c]	0.056
$k_{\theta Cl}$	~0.005 (rad)	0.071
$k_{\psi H}$	0.021(rad)[d]	0.032
$k_{\psi Cl}$	0.000(rad)	0.031

[a] Equilibrium position means the minimum points in potential energy surface and is described by polar coordinates. [b] In solid hydrogen chloride, k_{r1} is difficult to calculate theoretically, the harmonic potential is used for HCl molecule and k_{s1} is adjusted to give observed stretching frequency of B1 mode. If the force constant k_{s1} is 5.02(mdyne/Å), stretching ν_{B1} is too large (3058 cm⁻¹) and $\Delta \nu_{int}$ is 45 cm⁻¹. [c] Electrostatic repulsions between nearest H-atoms give this deviation. [d] Ito, Susuki, and Tokoyama (1969) concluded that the zigzag chain in ab plane is nonplanar. Wang et al. (1970) persisted that the zigzag hydrogen bonded -H-Cl-H chain is pushed out of plane in order to maintain lattice stability.

the other is asymmetry of the potential surface of Cl atoms. The cell constants, $a < b < c$, strongly suggest that HCl molecules in orthorhombic crystal form hydrogen bonds along the b-axis although the evidence of hydrogen bonds in this crystal is not clear. In this work, the potential surface of chlorine atom is remarkably asymmetric, and this asymmetry is responsible for the dipole-quadrupole and quadrupole-quadrupole interactions introduced in the other calculations.

In orthorhombic hydrogen chloride, the origin of the internal mode splitting is the interactions between HCl molecules along the $r2$ coordinate in ab plane. If k_{r2} is varied 0.1 mdyne/Å, then the change in $\Delta \nu_{int}$ is about 15~20 cm⁻¹ ($\Delta \nu_{int}/k_{r2}$ = 150 200 mdyne/Å cm). In the case of k_{r1}, $\Delta \nu_{int}/k_{r1}$ = 2~3 mdyne/Å cm. k_{s2} is sensitive to the interatomic interactions which participate in H-bond (H-Cl and Cl-Cl interaction along b-axis). $\Delta \nu_{int}$ was calculated by Ito, Susuki and Tokoyama[3] as 6 cm⁻¹, because they assigned small value to k_{s2}(0.059 mdyne/Å).

Grout and Leech[7] also failed to explain above splitting, $\Delta \nu_{int}$ = 3~12 cm⁻¹, although the influence of hydrogen bond was encountered in the calculation.

Grout and Leech[7] failed in explaining this splitting because the potential surface of Cl atom in the crystal is symmetric. Cl-Cl interactions in ab plane are very important because chlorine atoms are closely contacted in ab plane. In the other calculations, most of workers calculate internal and external modes separately because of small coupling between the intra and inter molecular motions due to the large difference in their vibrational frequencies. The polar coordinates representation used in this calculation is suitable for both internal and external mode calculations. Especially, this representation is reasonable for librational motions in crystals. The $r1$ and $r2$ coordinates are almost orthogonal, if the mass of H atom is neglected, then $\vec{k}_{r1} \cdot \vec{k}_{r2}/|k_{r1}| \cdot |k_{r2}|$ is nearly zero. Therefore any internal motions in ab plane can be described successfully.

There are many difficulties in comparing the calculated librational modes with observed frequencies because the assignment for the librational frequencies are different from worker to worker. For librational modes, ν_{B1} is 500 cm⁻¹(500[13], 496[11]), ν_{A2} is 260 cm⁻¹(214[3], 135[6]), ν_{A1} is 253 cm⁻¹(278[13], 296[11]), and ν_{B2} is 191 cm⁻¹(215[13], 337[6]). The summary of mode assignments are listed in Table 3 of ref. 7. In the case of translational modes, ν_{B1} is 121 cm⁻¹(109[11]), ν_{A1} is 52 cm⁻¹(89[6]), and ν_{A2} is 58 cm⁻¹(55[3]).

TABLE 3: The Lattice Vibrational Calculations and Experiments on the Orthorhombic Solid HCl

Assignments		Ito *et al.*		Sun *et al.*	Grout *et al.*		This work	Experiment	
Internal	B1	—[d]	(2734)[e]	—	2726[f]	(2728)[g]	2741 (3058)[h]	2745	
modes	A1	—	(2728)	—	2715	(2716)	2692 (3013)	2706	
Librational	B1	125	(502)	522	239	(323)	500	496[i]	(409)[b]
modes	A2	234	(214)	181	220	(232)	260	—	
	A1	111	(295)	269	175	(192)	235	296[i]	(290)[c]
	B2	0	(217)	384	273	(291)	198	215[k]	(337)[b]
Translational	B1	3	(103)	132	108	(99)	121	109[i]	(114)[b]
modes	A1	0	(90)	104	93	(88)	52	84[o]	(89)[b]
	A2	0	(55)	68	54	(53)	58	55[o]	(61)[b]

[a] Ito *et al.* (1969). [b] Sun and Anderson (1972). [c] Grout and Leech (1974). [d] Lattice vibrational calculation using general central force field. [e] Using adjusted force constant to give the best fit with the observed frequencies. [f] Point-ion AN model. [g] Point-ion NN model. [h] When k_{s1} is 5.20 mdyne/A. [i] Hornig and Osberg (1955). [j] Carlson and Friedrich (1971), [k] Arnold and Heastic (1967). [l] Anderson *et al.* (1964). Frequencies are in cm⁻¹.

Our calculation gives good results as a whole except v_{A2} in translational mode. This means that there are still difficulties in a potential form for expressing the intrachain interactions.

In this paper, the asymmetric potential functions are introduced in order to reproduce the observed cell parameters and to give physically realistic surface of potential. The polar coordinates representation is used in order to describe the motions of molecules in molecular crystals. As many authors have suggested quantum effects must be included in potential functions.

Acknowledgement. This work was supported in part by the Korea Research Center for Theoretical Physics and Chemistry and the Korea Science and Engineering Foundation. The authors wish to thank professor H. Kim in University of Missouri for the valuable discussions and suggestions of the vibrational study.

References

(1) E. Sandor and R.F.C. Farrow, *Nature*, **213**, 171 (1967).

(2) E. Sandor and R.F.C. Farrow, *Nature*, **215**, 1265 (1967).

(3) M. Ito, M. Susuki, and T. Tokoyama, *J. Chem. Phys.*, **50**, 2949 (1969).

(4) H. B. Friedrich and R. E. Carlson, *J. Chem. Phys.*, **53**, 4441 (1970).

(5) R. E. Carlson and H.B. Friedrich, *J. Chem. Phys.*, **54**, 2794 (1971).

(6) T. S. Sun and A. Anderson, *Chem. Phys. Letters*, **17**, 104 (1972).

(7) (a) P. J. Grout and J. W. Leech, *J. Phys.*, **C7**, 3245 (1974), (b) W. S. Tse, *Chem. Phys. Letters*, **112**, 524 (1984).

(8) P. N Ghosh, *J. Phys.*, **9**, 2673 (1976)

(9) V. Schettino and P.R. Salvi, *Chem. Phys.*, **41**, 439 (1979).

(10) D. F. Hornig and W. E. Osberg, *J. Chem. Phys.*, **4**, 662 (1955).

(11) A. Anderson, M. Gebbie, and S. H. Walmsley, *Molec. Phys.*, **7**, 401 (1964).

(12) R. Savoie and A. Anderson, *J. Chem. Phys.*, **44**, 548 (1966).

(13) G. M. Arnold and R. Haestie, *Chem. Phys. Letters*, **1**, 51 (1967)

(14) C. H. Wang and P. A. Fleury, *J. Chem. Phys.*, **53**, 2243 (1970).

(15) A. L. McClellen, "Tables of Experimental Dipole Moments", Freeman, San Francisco, 1963.

(16) Landolt-Bornstein, "Zahlenwerte and Funktion Vol. 1, Part 3", Springer-Verlag, Berlin, P. 510 (1951).

(17) *ibid*, "Zahlenwerte and Funktion Vol. 2, Part 4," Springer-Verlag, Berlin, P. 413 (1961).

(18) W. D. Gwinn, *J. Chem. Phys.*, **55**, 477 (1971).

The Study on the Physicochemical Properties of Fluid under High Pressure (II). The Effect of Pressure and Temperature on the Hexamethyl Benzene-Iodine Charge Transfer Complex in *n*-Hexane

Oh Cheun Kwun[†] and Jeong Rim Kim

Department of Chemistry, Hanyang University, Seoul 133, Korea (Received December 26, 1984)

The effect of pressure and temperature on the stabilities of the charge transfer complexes of hexamethyl benzene with iodine in *n*-hexane has been investigated by UV-spectrophotometric measurements. In this experiment the absorption spectra of mixed solutions of hexamethyl benzene and iodine in *n*-hexane were measured at 25, 40 and 60°C under 1, 200, 600, 1200 and 1600 bar. The equilibrium constant of the complex formation was increased with pressure while being decreased with temperature raising. Changes of volume, enthalpy, free energy and entropy for the formation of the complexes were obtained from the equilibrium constants. The red shift at higher pressure, the blue shift at higher temperature and the relation between pressure and oscillator strength were discussed by means of thermodynamic functions. In comparison with the results in the previous studies, it can be seen that the pressure dependence of oscillator strength has a extremum behavior in durene as the variation of ΔH or ΔS with the number of methyl groups of polymethyl benzene near atmospheric pressure in the previous study. The shift or deformation of the potential in the ground state and in the excited state of the complexes formed between polymethyl benzene and iodine was considered from the correlation between the differences of the electron transfer energies and the differences of free energies of the complex formation for the pressure variation.

Introduction

In part I', we discussed the thermodynamic properties on the formation of electron donor-acceptor complexes formed between polymethyl benzene and iodine in *n*-hexane and came to conclusion that the stabilities of the charge transfer complexes having iodine in common could mainly be affected by the positive inductive effect because the steric hindrance effect of polymethyl benzene is nearly destroyed by the strong external restraints at higher pressure.

This paper reports a study of iodine solutions under high pressures which was undertaken in an effort to learn more about molecular complexes in general and, specifically, more about the polymethyl benzene-iodine complexes. in the earlier works[1-6], since the effect of pressure and temperature on the charge transfer absorption of the complexes of six polymethyl benzenes with iodine had been investigated in *n*-hexane, we have now extended our measurements to include electron donor-