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Ab Initio SCF-SDCI Prediction of Type II Spectra and Geometry of $(ClHCl)^-$ Hydrogen Bond Complex. I. One Dimensional Vibrational Analysis

Toshikazu Saitoh,* Kazuhide Mori, Kotoku Sasagane, and Reikichi Itoh
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160
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Ab initio SCF(self-consistent field)-SDCI(single and double configuration interaction) calculations are presented on HCl_2^-. Applied basis sets are 4-31G, 4-31G(**) (no 3d-polarization functions on Cl atoms and 2p-polarization functions on H atom), 4-31G** (addition of polarization functions both on Cl and H atoms) and the split basis by Dunning (Cl/12s9p)(H/4s)→[Cl/6s5p][H/2s] with the addition of diffuse functions and/or polarization functions. Vibrational and geometrical analyses are performed on the Cl–Cl potential surface under symmetry conservation, and then on the proton potential surface at optimized R_{Cl-Cl} position. After potential interpolation by the continuous quadratic functions which reconstruct the calculated potential values on all mesh points, the quantal vibrational analysis is perfomed by the Störmer-Levy difference method. Discussion is made on the experimental confusion about the assignment of type II spectra of HCl_2^- as ν_3 mode in an argon matrix by the selection of basis set and of CI matrix expansion. Whereas the calculations in a primitive size proposes the double minimum potential surface of proton and type II spectra in $\approx$700 cm^{-1} region as ν_3 (which corresponds to the experimental data by Evans and Lo (1966) and Ault (1975)), the extended calculations (*i.e.* the large basis sets and the great number of CI matrix expansion) reduce the central barrier of the proton potential and then conclude the IR absorption in 1000—1100 cm^{-1} region as ν_3 in the type II spectra (which corresponds to the experimental results of $CsCl \cdot 1/3\ [H_3O^+HCl_2^-]$ by Schröder (1970) and Smith (1973)).

It is the well known fact that the hydrogen bonded hydrogen dihalide ions $(XHX)^-$ and $(XHY)^-$ provide the useful informations about the symmetric and the asymmetric hydrogen bonds. Earlier investigations on this kind of molecules are focusd on $(FHF)^-$, which is one of the strongest hydrogen bonds (Hydrogen bond energy is 58 ± 5 kcal mol^{-1}).[1,2] Neutron diffraction,[3,4] neutron inelastic scattering,[5] and IR-Raman studies[6-8] predicted that HF_2^- ions in $NaHF_2$ and KHF_2 crystals have symmetric linear triatomic structure ($D_{\infty h}$ symmetry) with single minimum proton potential. Singh ans Wood (1968, 1969)[9] estimated the vibrational structure of this ion using the variational method for the empirical potential surface. Almlöf (1972)[10] calculated the *ab initio* SCF-MO potential surface of linear $(FHF)^-$ ion in the two vibrational degrees of freedom and succeeded in the assignment of the vibrational spectra with high accuracy. Jiang and Anderson (1973)[11] and Barton and Thorson (1979)[12] also performed the vibrational studies on $(FHF)^-$ by one-dimensional approach and adiabatic approximation respectively on the semi-empirical (Lippincott-Schröder) potential which was fitted to the MO potential by Almlöf. They also gave supports to the experimental accounts on the structure and properties of $(FHF)^-$ ion. Though the anions in KHF_2 and $NaHF_2$ have symmetric structures, $(FHF)^-$ in *p-toluidinium hydrogen difluoride* has an asymmetric structure affected by an enviroment. R_{F-F} is 2.26 Å in both symmetric salts and asymmetric salt. R_{H-F} distances in asymmetric $(FHF)^-$ ion are 1.025 and 1.235 Å.[13]

The hydrogen bond energies of $(ClHCl)^-$, $(BrHBr)^-$, $(IHI)^-$, and $(ClHBr)^-$ are 18.9,[14] 11.6, 7.3, and 9.1[15] kcal mol^{-1} respectively. This implies that the structures and spectra of those ions are readily influenced by the molecular enviroment. Waddington (1958)[16] reported the IR spectra of $(CH_3)_4N^+HCl_2^-$ and suggested that $(ClHCl)^-$ has the linear symmetric structure on the basis of the similarity of the spectra with that of $(FHF)^-$. Evans and Lo (1966)[17] obtained two different types of spectra for salts of HCl_2^- and $(ClHBr)^-$. They reported the IR spectra of $Cs^+HCl_2^-$ in solid phase and a series of $R_4N^+HCl_2^-$ type solutions. Type I spectra are observed for $Cs^+HCl_2^-$, $(CH_3)_4N^+HCl_2^-$, and n-$(C_3H_7)_4N^+HCl_2^-$. There are two intense broad peaks at 1520—1670 cm^{-1} and near 1200 cm^{-1} and weak band near 220 cm^{-1} in the type I spectra. Type II spectra are obtained for $(C_2H_5)_4N^+HCl_2^-$, n-$(C_3H_7)_4N^+HCl_2^-$, and n-$(C_5H_{11})_4N^+HCl_2^-$. Type II salts indicate intense and broad band at 700—800 cm^{-1} which is extending from 600 to 1300 cm^{-1} region and consecuted to another weak and broad peak at 1000—1050 cm^{-1}. Evans and Lo predicted that $(ClHCl)^-$ ions in type I salts are in the asymmetric ($C_{\infty h}$ or C_s) structures and type II salts are in the symmetric ($D_{\infty h}$ or C_{2v}) structures. Isotope frequency ratio of ν_3 suggests that the proton potentials are single minimum both in type I and type II salts. Nibler and Pimentel (1967)[18] also predicted that type I HCl_2^- ion in $Cs^+HCl_2^-$ salt is not in the symmetric structure by the group theory consideration on the infrared activities and by the analogy of IR spectra between Cs^+ClHBr^- and $Cs^+HCl_2^-$. Neutron scattering studies on $Cs^+HCl_2^-$ by Stirling *et al.* (1970),[19] Smith *et al.* (1973),[20] and Howard *et al.* (1979)[21] also gave supports to the prediction of the noncentrosymmetric structure of type I salts. The definitive structural data on a dichloride salt is obtained for $CsCl \cdot 1/3\ [H_3O^+HCl_2^-]$ by X-ray diffraction experiment (Schröder and Ibers (1966)[22]). The dichloride ions occur as strings$\cdots(ClHCl)^-\cdots(ClHCl)^-\cdots$, parallel to the hexagonal axis in the structure. R_{Cl-Cl} distance is 3.14 ± 0.02 Å. Schröder (1970)[23] also obtained type II spectra of this crystal. IR and Raman data predict the centrosymmetric structure for $(ClHCl)^-$ ion. ^{35}Cl Neutron Quadrupole Resonance (NQR) spectroscopy of $(ClHCl)^-$ salts show two different ^{35}Cl frequencies for

type I and type II salts. Ludman *et al.* (1970)[24] obtained ^{35}Cl NQR spectra on $(CH_3)_4N^+HCl_2^-$, $Cs^+HCl_2^-$ (type I salts) and on $(C_2H_5)_4N^+HCl_2^-$, $CsCl\cdot 1/3\,[H_3O^+HCl_2^-]$ (type II salts). ^{35}Cl frequencies of type I salt are classified into the group which indicate about 20 MHz and type II are about 12 MHz. Dixon *et al.* (1975)[25] obtained the theoretical value of ^{35}Cl NQR frequency by *ab initio* SCF-MO calculation with the use of minimal STO basis functions. Calculated values are 12.6 MHz for $(FHCl)^-$ and 37.5 MHz for $(ClHCl)^-$. Thomson *et al.* (1975)[14] also calculated the potential surface and ^{35}Cl NQR frequency for $(ClHCl)^-$ by *ab initio* SCF-MO applying STO double zeta+polarization basis functions. Their results are that;

(i) proton potential surface is flat (nearly single minimum) at $R_{Cl-Cl}=3.14$ Å (which corresponds to the experimental R_{Cl-Cl} distance of $CsCl\cdot 1/3\,[H_3O^+HCl_2^-]$), the proton localizes in the center of mass and then ^{35}Cl NQR frequency is 13.11 MHz,

(ii) proton potential has two equivalent minima at $R_{Cl-Cl}=3.22$ Å (which corresponds to the experimental R_{Cl-Cl} distance in $Cs^+HCl_2^-$), the proton localizes in either minimum and ^{35}Cl NQR frequency is 21.0 MHz in the two equivalent minima at $R_{HCl}=1.365$ Å.

It is assured by these experimental and theoretical results that HCl_2^- ions in type I salts are in the noncentrosymmetric structures and type II are in the centrosymmetric ones.

However on the assignments of ν_2 and ν_3 modes in type II spectra there are some disagreements among the experimental results. Evans and Lo assigned the ν_2 and ν_3 modes of $n\text{-}(C_5H_{11})_4N^+HCl_2^-$ as 1050 and 780 cm^{-1} respectively. Whereas Schröder (1970)[23] predicted $\nu_2=500$—$1200\ cm^{-1}$ and $\nu_3=1050$—$1200\ cm^{-1}$ for $CsCl\cdot 1/3\,[H_3O^+HCl_2^-]$. (The overlap with the ν_2 mode of H_3O^+, 1150 cm^{-1}, prevented the detailed assignments of ν_2 and ν_3 modes of $(ClHCl)^-$.) Neutroninelastic scattering studies of types II salts[20] predicted $\nu_2=795\ cm^{-1}$, $\nu_3=1275\ cm^{-1}$ for $(C_2D_5)N^+(CD_3)_3HCl_2^-$ and $\nu_2=795\ cm^{-1}$ for $CsCl\cdot 1/3\,[H_3O^+HCl_2^-]$. The ν_1 mode of centrosymmetric anion should be Raman active and IR inactive. Though type II spectra by Evans and Lo indicate the weak ν_1 absorption peak in the far-IR region (250 cm^{-1}), Schröder observed ν_1 mode as Raman active and far-IR inactive. The ν_1 mode by neutron inelastic scattering spectra[20] were 218 cm^{-1} for $(C_2D_5)N^+(CD_3)_3HCl_2^-$ and 275 cm^{-1} for $CsCl\cdot 1/3\,[H_3O^+HCl_2^-]$. Recently Ault and Andrews (1975)[26] reported a series of IR and Raman spectra of $M^+HCl_2^-$ (M=alkali metal) in the argon matrix. For example the results for $Rb^+HCl_2^-$ are $\nu_1=250\ cm^{-1}$ (Raman), $\nu_2=600\ cm^{-1}$ (IR), and $\nu_3=729\ cm^{-1}$ (IR). This encourage the assignments by Evans and Lo. ν_3 spectra of this type had been explained as those of HCl_2^- radical. Noble and Pimentel (1968)[27] obtained the IR spectra of $HCl/Cl_2/Ar$ matrix which indicate absorption peaks at 696.4 cm^{-1} (ν_3) and 955.6 cm^{-1} ($\nu_1+\nu_3$). However the later study (Milligan and Jacox (1970)[20]) by vacuum ultraviolet photolysis of HCl/Ar matrix provided the same spectra; $\nu_3=696\ cm^{-1}$ and $\nu_1+\nu_3=956\ cm^{-1}$, which were accounted as those of HCl_2^- ion. Type II spectra of alkali halide salts are consistent with those by Milligan and Jacox, and by Evans and Lo. The isotope frequency ratios ν_3^H/ν_3^D by Ault are almost the same those of harmonic oscillators. This is indicative of the single minimum potential for the vibration of proton. Since ν_1 is only Raman active, the structure of $ClHCl^-$ line is expected to have $D_{\infty h}$ symmetry.

The purpose of this paper is to determine the assignments of type II spectra of $(ClHCl)^-$ ion in the centrosymmetric structure by the theoretical consideration. We calculate the vibrational potential surfaces of Cl–Cl and proton by the *ab initio* SCF-SDCI method applying Gaussian basis sets. We still calculated the quantal vibrational eigenvalues for ν_1 and ν_3 modes by one dimensional Störmer-Levy difference method. In the next section we review the computational details, *i.e.* the selection of the basis sets, single and double excitations from the single reference state configuration interaction (SDCI) method, interpolation method of potential surface and quantal vibrational analysis (Störmer-Levy method). In the result section the calculated results are presented. In the final section we shall consider in the level of discussion the assignment of ν_3 in the type II spectra of centrosymmetric $(ClHCl)^-$ anion.

Computational Details

The AO basis sets employed in the present calculation are seven types of split valence ones. To clarify the types of basis sets we employ the following expressions,

(i) the well known 4-31G basis sets,[29]

(ii) 4-31G(**) *i.e.* we denote the addition of 2p polarization functions on H atom to 4-31G basis sets,

(iii) 4-31G** *i.e.* the addition of 3d polarization functions on Cl atoms and of 2p polarization functions on H atom,

(iv) [6s5p](**) basis for chlorine in a (6,3,1,1,1,1/5,1,1,1,1) contraction (*i.e.* [Cl/6s5p])[30] and hydrogen in a (3,1/1) contraction (*i.e.* [H/2slp]),[31]

(v) [6s5p](**)+diff basis sets with the addition of diffuse functions on Cl atoms to [6s5p](**) basis sets,

(vi) [6s5p]** basis sets with the addition of 3d polarization functions on Cl atoms to [6s5p](**) basis sets, and

(vii) [6s5p]**+diff basis sets with the addition of 3d polarization functions and diffuse functions on Cl atoms to [6s5p](**) basis sets.

The orbital exponents of 2p polarization functions of hydrogen are $\zeta_p=1.0$ (in 4-31G(**) and 4-31G**),[32] $\zeta_p=0.75$ (in Dunning basis sets)[33] which is optimized for HCl molecule. The exponents of 3d polarization functions are $\zeta_d=0.6$ for all basis sets, which is optimized for [Cl/6s4p] basis sets of HCl molecule.[33] Literature cited ζ_d value for Cl atom is 0.619 which is obtained by Ahlrichs equation, $\zeta_d=0.77\cdot Z-0.69$ (for $11\leqq Z\leqq 18$).[34] The employed ζ_d value will be a reasonable selection. The exponent of 3p diffuse function has the value $\zeta_{3p}=0.049$ for all Cl atoms.[35] SCF calculations are carried out with the use of GAUSSIAN 70 program[36] for 4-31G basis set calculations and with GAUSSIAN 76 program[32] for other basis sets in a double precision on IMS HITAC M-200H computers.

The CI calculations are in a single and double excitations from single reference state configuration interaction (SDCI) type[37] for 4-31G and 4-31G(**) calculations and in a direct SDCI (CIMI) type[38] for other calculations. All configuration state functions (CSF's)are treated with a common sets of MO's from the SCF solution. The valence occupied MO's of the SCF solution consist of $(\sigma_g)^2(\sigma_u)^2(\sigma'_g)^2(\pi_g)^4(\pi_u)^4(\sigma'_u)^2$ MO's. CSF's are generated from the pair of single and double excitations from the occupied MO's to the virtual MO's. For all calculations the size of CI matrix is selected so that the occupied MO's are restricted to the valence MO's only and the virtual MO's are from the lower state to a required state in consideration of the results. Another corrections to the CI energies are generated using Davidson's formula[39] for estimating the contribution of quadrupole excitations. Standard SDCI program is linked both to GAUSSIAN 70 and 76 SCF program and direct SDCI program is linked only to the latter.

The coordinates of the system are taken as to make two dimensional potential surface in which the vibration of Cl–Cl and proton on Cl–Cl axis occur. The origin of the potential is taken at the center of Cl–Cl. The interpolation of the MO potential is inevitable for the quantal vibrational analysis for the lack of mesh points. We employed the continuous quadratic functions interpolation method that is to interpolate the required potential values for the difference method. The procedure of the calculation starts with the computation of the MO potential value P_n at $N+1$ points S_n $(0 \leqq n \leqq N)$. Three pairs of potential data (S_{n-1}, P_{n-1}), (S_n, P_n), and (S_{n+1}, P_{n+1}) in a series provide one approximate potential function $f_n(x)=a_nx^2+b_nx+c_n$ which generates a series of mesh point values in a region $S_n \leqq x \leqq S_{n+1}$. The coefficients a_n, b_n, and c_n are given by,

$$a_n = \frac{P_{n-1}(S_{n+1}-S_n)-P_n(S_{n+1}-S_{n-1})+P_{n+1}(S_n-S_{n-1})}{(S_{n+1}-S_n)(S_{n+1}-S_{n-1})(S_n-S_{n-1})}, \quad (1)$$

$$b_n = \frac{P_n-P_{n-1}}{S_n-S_{n-1}} + a_n(S_{n-1}+S_n), \quad (2)$$

and

$$c_n = \frac{P_nS_{n-1}-P_{n-1}S_n}{S_{n-1}-S_n} + a_nS_{n-1}S_n (\text{for } 1 \leqq n \leqq N-1). \quad (3)$$

The potential value $h(x)$ (where $S_n \leqq x \leqq S_{n+1}$) are evaluated by the average of $f_n(x)$ and $f_{n+1}(x)$, which are generated succesively by the following equation,

$$h(x) = \frac{(S_{n+1}-x)f_n(x)+(x-S_n)f_{n+1}(x)}{S_{n+1}-S_n}$$
$$(\text{for } S_n \leqq x \leqq S_{n+1} \text{ and } 1 \leqq n \leqq N-1). \quad (4)$$

The potential values for $x<S_1$ and $x>S_{N-1}$ are extrapolated by the start and the final functions $f_1(x)$ and $f_N(x)$ respectively. The coordinates of the system are taken as the same ones by Almlöf[10] and Janoschek *et al.*[40] That is, the origin is centered on the $(Cl(1)–H–Cl(2))^-$ ion and the symmetry coordinates $R_{Cl-Cl}=R_{Cl(1)-H}+R_{Cl(2)-H}$ and $r_H=1/2\ (R_{Cl(1)-H}-R_{Cl(2)-H})$ are employed. This is one of the molecular Jacobi coordinates for symmetric linear triatomic system and is called as "molecular coordinates".[12] The reduced masses of two vibrational degrees of freedom are taken as $\mu_1=M_{Cl}/2$ and $\mu_3=2M_HM_{Cl}/(2M_{Cl}+M_H)$.

The quantal vibrational analysis is given by the Störmer–Levy difference method.[43] This method gives an accurate solution even in the case of discrete potential values in a numerical form with the great number of mesh points and with the proper selection of the position to start the initial guess at outside enough of the potential well. Vibrational analysis is performed on R_{Cl-Cl} surface and r_H surface. Initial point, final point, and the mesh width ΔR are taken as (2.7 Å, 3.8 Å, 0.001 Å) in R_{Cl-Cl} direction and (−0.914 Å, +0.886 Å, 0.001 Å) in r_H direction. The number of calculated MO potential values are 8 points in R_{Cl-Cl} direction and 11 points (21 points up to total by the symmetry) in r_H direction at optimized R_{Cl-Cl} distance.

Results

Figure 1 illustrates the correction energy variation in R_{Cl-Cl} direction. The effect of basis set extension is in the order 4-31G**>4-31G(**) both in magnitude and in R_{Cl-Cl} dependence of the shift value. This implies that the "steepness" of Cl–Cl potential curve is in the order 4-31G>4-31G**>4-31G(**) and the equilibrium

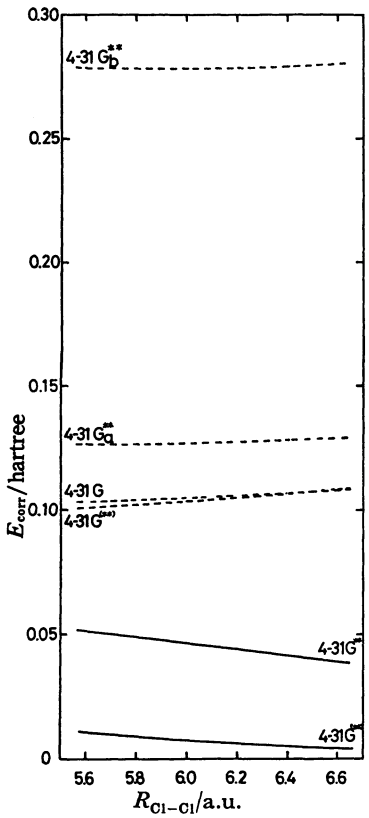

Fig. 1. Correction energy values of Cl–Cl direction on basis set expansion for 4-31G basis sets and on CI. $E_{corr}=E_T$(4-31G SCF)$-E_T$ for SCF calculation and $E_{corr}=E_T$(SCF)$-E_T$(CI) (in the same basis set) for CI calculation. ——: SCF calculation and ------: CI calculation. 4-31G$_a^{**}$ denotes that the number of CI matrix expansion is 4005 and 4-31G$_b^{**}$ denotes that the expansion is 13041. (1 a.u.$=5.291677\times10^{-11}$ m, 1 hartree$=4.359814\times10^{-18}$ J).

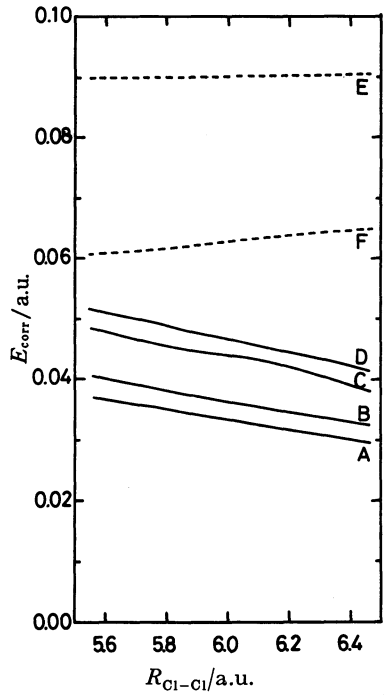

Fig. 2. Correction energy values of Cl–Cl direction on basis set expansion and CI for [6s5p] basis sets. $E_{corr} = -1.0 + E_T(\text{4-31G SCF}) - E_T$ for SCF calculations and $E_{corr} = E_T(\text{SCF}) - E_T(\text{CI})$ for CI calculations. ——: SCF calculation and ------: CI calculation. A: [6s5p]$^{(**)}$ SCF, B: [6s5p]$^{(**)+diff}$ SCF, C: [6s5p]** SCF, D: [6s5p]$^{**+diff}$ SCF, E: [6s5p]$^{(**)}$ CI (the number of CI matrix expansion is 5565), and F: [6s5p]$^{**+diff}$ CI (CI expans.=5565).

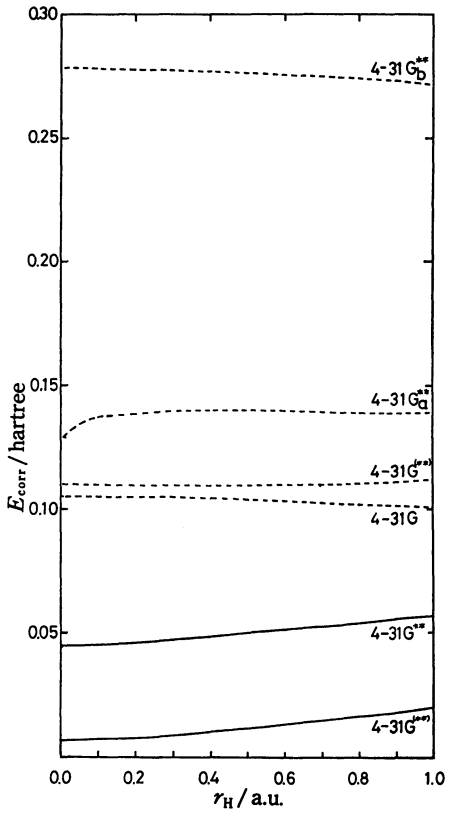

Fig. 3. Correction energy values on proton displacement from the symmetric position. $E_{corr} = E_T(\text{4-31G SCF}) - E_T$ for SCF calculations and $E_{corr} = E_T(\text{SCF}) - E_T(\text{CI})$ for CI calculations (in the same basis set). ——: SCF calculation and ------: CI calculation. 4-31G$_a^{**}$ denotes that the number of CI matrix expansion is 4005 and 4-31G$_b^{**}$ denotes that the expansion is 13041.

distance for Cl–Cl is in the order 4-31G>4-31G$^{(**)}$>4-31G**. Though the effect of CI is greater than that of basis set extension, R_{Cl-Cl} dependence of CI correction energy for the same basis set is rather small and in increase with the increase of R_{Cl-Cl}. This also implies that R_{Cl-Cl} potential become "gentle-sloping" in the long Cl–Cl distance and then lengthen the equilibrium Cl—Cl distance. The slope of CI potential curve is expected to be in the order 4-31G**>4-31G>4-31G$^{(**)}$. The effect of basis set extension cancel the effect of CI on the sloping of the potential. Thus the

TABLE 1. CALCULATED VIBRATIONAL FREQUENCIES AND OPTIMIZED GEOMETRY OF HCl_2^- (4-31 G, 4-31 G$^{(**)}$, and 4-31 G** basis sets)

Basis set	Method	ν_1 / cm^{-1}	ν_3		ν_H/ν_D	R_{Cl-Cl} / Å	Min.pos.[a] / Å	Barrier height / cm^{-1}
			ν_H / cm^{-1}	ν_D / cm^{-1}				
4-31 G	SCF	274.0	1044	688.0	1.56	3.222	0.0	0.0
	CI[b]	289.6	1089	726.5	1.50	3.264	0.0	0.0
	SDQ	288.9	1112	745.4	1.49	3.274	0.0	0.0
4-31 G$^{(**)}$	SCF	266.3	553.0	278.6	1.99	3.158	±0.228	404.4
	CI[c]	257.4	686.2	387.1	1.77	3.227	±0.194	205.5
	SDQ	269.8	711.5	408.7	1.74	3.234	±0.189	115.9
4-31 G**	SCF	350.2	867.7	521.3	1.66	3.132	±0.145	88.6
	CI(1)[d]	337.9	485.9	196.6	2.47	3.143	±0.194	2826
	(2)[e]	352.3	1050	672.2	1.56	3.134	0.0	0.0
	SDQ(1)	334.2	444.4	156.4	2.84	3.149	±0.195	3058
	(2)	340.6	1094	709.1	1.54	3.140	0.0	0.0

a) Minimum position of the proton displacement potential at optimized R_{Cl-Cl} distance (displacement value from the central position). b) CI matrix expansion is 3321. R_{Cl-Cl}=3.228 Å. c) CI matrix expansion is 3321. R_{Cl-Cl}=3.228 Å. d) CI matrix expansion is 4005. R_{Cl-Cl}=3.149 Å. e) CI matrix expansion is 13041. R_{Cl-Cl}=3.140 Å.

TABLE 2. CALCULATED VIBRATIONAL FREQUENCIES AND OPTIMIZED GEOMETRY OF HCl_2^- ([6s5p](**), [6s5p](**)+diff, [6s5p]**, and [6s5p]**+diff basis sets)

Basis set	Method	ν_1 / cm^{-1}	ν_3		ν_H/ν_D	R_{Cl-Cl} / Å	Min. pos.[a] / Å	Barrier height / cm^{-1}
			ν_H / cm^{-1}	ν_D / cm^{-1}				
[6s5p](**)	SCF	342.3	723.3	401.6	1.80	3.157	±0.190	254.9
	CI[b]	334.2	826.4	493.0	1.68	3.161	±0.152	92.4
	SDQ	323.9	849.7	513.2	1.66	3.193	±0.147	66.9
[6s5p](**)+diff	SCF	342.9	688.3	371.9	1.85	3.155	±0.197	351.2
	CI[c]	326.8	1177	789.7	1.49	3.188	0.0	0.0
	SDQ	323.9	1214	821.1	1.48	3.193	0.0	0.0
[6s5p]**	SCF	351.4	892.4	538.2	1.66	3.143	±0.142	84.2
[6s5p]**+diff	SCF	352.1	860.4	510.7	1.69	3.141	±0.150	118.2
Jiang and Anderson(1974)	Semiempirical	—	762	455	1.67	3.133	±0.20	81
Exptl	($Na^+(HCl_2)^-$)	302	658	436	1.51	(3.22)[d]	—	—
	($K^+(HCl_2)^-$)	250	736	498	1.48	—	—	—
	($Rb^+(HCl_2)^-$)	250	729	512	1.42	—	—	—
	($Cs^+(HCl_2)^-$)	250	723	507	1.42	(3.14)[e]	—	—

a) Minimum position of the proton displacement potential at optimized R_{Cl-Cl} distance. b) CI matrix expansion is 5565. R_{Cl-Cl} = 3.157 Å. c) CI matrix expansion is 5565. R_{Cl-Cl} = 3.155 Å. d) For $(CH_3)_4N^+HCl_2^-$. e) For CsCl·1/3 [$H_3O^+HCl_2^-$].

basis set extension is expected to play an important role on the spacing of the vibrational energy to the extent of CI expansion terms.

Figure 2 shows the correction energies on Dunning basis sets. SCF results suggest that Dunning basis sets make the Cl–Cl potential "steeper" and make the equilibrium distance shorter in comparison with 4-31G SCF potential. The relation between SCF and CI among the SCF results for different basis sets are the same in 4-31G system. The CI correction value in the same number of CI expansion terms become smaller for the basis set extension from [6s5p](**) to [6s5p](**)+diff. This indicates that the greater number of CI matrix expansion for the smaller basis set is the better selection to obtain the potential surface which involves the greater CI correction energy. Since R_{Cl-Cl} dependence of CI correction energy is relatively small, it is expected that the greater ν_1 value and shorter R_{Cl-Cl} distance appear in every calculation on Dunning basis sets in comparison with 4-31G results.

Tables 1 and 2 show calculated vibrational frequencies and optimized geometry of HCl_2^- for the basis sets (i)—(iii) and (iv)—(vii). In Tables 1 and 2 the above-mentioned tendencies are veirfied numerically. In Table 1 ν_1 values are in the order 4-31G** >4-31G ≳4-31G(**) in SCF calculation. Since ν_1 values from CI potential are the sum of basis set contribution and CI contribution to the potential curvature around the equilibrium distance, the ν_1 variation become the complicated order. ν_1 values by CI are greater than those by SCF in 4-31G and 4-31G** CI(2). But the reverse relations are detected in 4-31G(**) and 4-31G** CI(1). In every calculation SDQ potentials provide no considerable shift in ν_1 values. R_{Cl-Cl} distances are also in the order 4-31G>4-31G(**)>4-31G** in SCF calculations. In all basis sets in Table 1 R_{Cl-Cl} distances are in the order SCF>CI>SDQ. The competing contributions from basis set extension and CI and/or SDQ are indicated characteristically in Table 1. In Table 2 the effect of basis set extension makes ν_1 value greater The addition of diffuse function gives no significant shift on ν_1 value. Whereas the addition of 3d polarization functions on Cl atoms provides the greater ν_1 values. ν_1 values in all calculations correspond with the results for 4-31G**. Even in the case of [6s5p](**) basis set ν_1 value is 37% greater than the experimental value 250 cm^{-1}. Whereas ν_1 values by 4-31G and 4-31G(**) SCF are only about 10% greater than the experimental value. Thus the basis set extension in every calculation seems to make the poorer fits of calculated ν_1 values to the experimental ones. Calculated equilibrium R_{Cl-Cl} distances show the same tendency as in 4-31G in the basis set extension. R_{Cl-Cl} distances are in the order [6s5p]**+diff<[6s5p]**<[6s5p](**)+diff<[6s5p](**) in SCF calculation. And the order SDQ>CI>SCF are detected for the R_{Cl-Cl} equilibrium distances by [6s5p](**) and [6s5p](**)+< basis sets. Diffuse functions also make no significant effect on the equilibrium R_{Cl-Cl} distance. The competing relations between basis set extension and CI are also recognized in the calculations by Dunning basis sets. Both 4-31G**SDQ(2) and [6s5p]**+diff SCF calculations provide the best fits to the experimental R_{Cl-Cl} distance for CsCl·1/3 [$H_3O^+HCl_2^-$]. These results imply that the best calculation may be attained either by the small basis set and large scale CI calculation or by the large basis SCF calculation.

Figure 3 indicates the variation of correction energy in the direction of r_H. In the central region the potential is mainly depressed by CI correction energy in comparison with the SCF potential. Thus CI reduces the central barrier. But the 4-31G$_a$** result shows the anomalous depression of correction energy around the central position. This increases the anomalous barrier

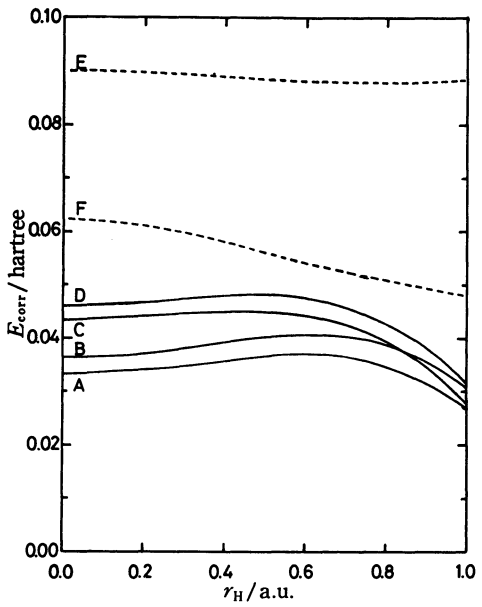

Fig. 4. Correction energy values (for Dunning's basis sets) on proton displacement from the central position. $E_{corr}=E_T$(4-31G SCF)$-E_T$ for SCF calculation and $E_{corr}=E_T$(SCF)$-E_T$(CI) for CI calculation (in the same basis set). The effects of basis set expansion are shown by —— and those of CI are shown by -------. A: [6s5p]$^{(**)}$ SCF, B: [6s5p]$^{(**)+diff}$ SCF, C: [6s5p]** SCF, D: [6s5p]$^{**+diff}$ SCF, E: [6s5p]$^{(**)}$ CI (the number of CI matrix expansion is 5565), F: [6s5p]$^{(**)+diff}$ CI (CI expans.=5565).

height. The reason for this will be discussed in the next section. In comparison with the relatively small change of CI correction energies on proton displacement, the correction to 4-31G SCF potential by the introduction of polarization function indicate the greater change on proton displacement. Slope of SCF correction curve is in the order 4-31G$^{(**)}$>4-31G**. Since the correction values by polarization functions are in the minimum at the symmetric position, SCF potentials for 4-31G$^{(**)}$ and 4-31G** are lowered in the asymmetric regions. This makes the central barrier greater and then makes ν_1 value smaller. Table 1 shows the numerical supports of these tendencies. The barriers come to be 404.4 and 88.6 cm^{-1} at 4-31G$^{(**)}$ SCF and 4-31G** SCF potentials respectively. The barrier height of 4-31G$^{(**)}$ SCF potential is reduced to be 205.5 and 115.9 cm^{-1} by introducing CI and SDQ respectively. In 4-31G calculation the barrier vanishes by CI(2) and SDQ(2) calculations. Though ν_3 values are about 1050 cm^{-1} in cases of single minimum potential, they decreased to be 550—870 cm^{-1} in double minimum potentials. The shift of ν_3 value for the basis set extension is in the order 4-31G>4-31G**>4-31G$^{(**)}$ and for the methods is in the order SDQ>CI>SCF. Exception is detected in the calculation of 4-31G** CI(1) and SDQ(1), in which the anomalous central barriers exist because of small number of CI matrix expansion.

Figure 4 shows the correction energy values on proton displacement from the symmetric position for the group of Dunning basis sets. The contribution from 3d polarization functions on the correction energy show the maximum at r_H=0.5 a.u. and is reduced in the highly asymmetric region. Whereas the contribution from the diffuse functions seems to be in nearly constant value in all regions. CI correction values are diminished in the asymmetric region and the value for [6s5p]$^{(**)+diff}$ (curve F) is smaller than that for [6s5p]$^{(**)}$ (curve E) in the same number of CI expansion terms and the curve E decreases in the asymmetric region. This implies the size of CI is not sufficient in [6s5p]$^{(**)+diff}$ CI calculation. These trends are also verified by the numerical results in Table 2. All of SCF potentials indicate double minimum shapes. The barrier heights by the SCF calculations are in the order [6s5p]$^{(**)+diff}\gtrsim$[6s5p]$^{(**)}$ >[6s5p]$^{**+diff}\gtrsim$[6s5p]**. The barrier heights for the methods are in the order SCF>CI>SDQ for [6s5p]$^{(**)}$ calculation. The barrier height for [6s5p]** or [6s5p]$^{**+diff}$ is nearly the same for 4-31G**.

ν_3 varies from 688.3 cm^{-1} to 892.4 cm^{-1} in SCF calculations. The contribution of 3d polarization functions adds about 100 cm^{-1} to the ν_3 values without 3d polarization functions. Single minimum potentials for [6s5p]$^{(**)+diff}$ CI and SDQ make ν_3 greater than 1100 cm^{-1}. The effect of diffuse functions on ν_3 is not significant. Whereas CI and SDQ contributions make ν_3 slightly greater than that by SCF value in [6s5p]$^{(**)}$ calculation. The experimental ν_3 values for $M^+HCl_2^-$ (M=alkali metal) varies from 658 to 736 cm^{-1}. Theoretical results by Jiang and Anderson[11] are ν_3=762 cm^{-1} and R_{Cl-Cl}=3.133 Å, which are well corresponding with the experimental results. The value of barrier height 81 cm^{-1} by Jiang and Anderson corresponds well with our results by 4-31G** SDQ, 4-31G** SCF [6s5p]$^{(**)}$ CI, [6s5p]** SCF, and [6s5p]$^{**+diff}$ SCF. R_{Cl-Cl} value by 4-31G$^{(**)}$ is greater than the experimental ones. Results by above-mentioned basis sets except for 4-31G$^{(**)}$ seem to show good agreements with the experimental values not only in R_{Cl-Cl} but also in ν_3 value and the barrier height. However the isotope frequency ratios ν_3^H/ν_3^D are in poorer agreements with the experimental values. The experimental ones show nearly the harmonic values. But the above-mentioned values show the greater isotope frequency ratios about 1.7—1.9. Though the values for the single minimum potential show better fits to the experimental ν_3^H/ν_3^D values, ν_3^H is about 300 cm^{-1} greater than the experimental ones. The calculated results have lead us to the complicated situation in which the alternative relations exist between the small ν_3 value and the fit of ν_3^H/ν_3^D. This is the critical point for the explanation of the state of isolated HCl_2^- ion; *i.e.* whether isolated HCl_2^- has double minimum potential or single minimum one along r_H axis. Experimental R_{Cl-Cl} values of HCl_2^- are obtained for $(CH_3)_4N^+HCl_2^-$ and CsCl·1/3 [H_3O^+ HCl_2^-] crystals. The longer experimental R_{Cl-Cl} value is 3.22 Å for $(CH_3)_4N^+HCl_2^-$ which corresponds with the asymmetric bond. And the shorter experimental R_{Cl-Cl} value is 3.14 Å for CsCl·1/3 [$H_3O^+HCl_2^-$], which agrees well with the results by 4-31G**, [6s5p]**, and [6s5p]$^{**+diff}$. Experimental ν_3 value of type II spectra for n-$(C_5H_{11})_4N^+HCl_2^-$ is obtained by Evans and Lo as 780 cm^{-1} and for CsCl·1/3 [$H_3O^+HCl_2^-$] is predicted as 1050—1200 cm^{-1} by Schröder. Calculated

TABLE 3. CALCULATED HYDROGEN BOND ENERGY of HCl_2^- (SCF CALCULATION)
(1 kcal mol^{-1} = 4.184 × 10^3 J mol^{-1})

Basis set	E_{min} / hartree	E_{400}[a] / hartree	ΔE / kcal mol^{-1}	Vibrational correction / cm^{-1}	ΔE_{coor} / kcal mol^{-1}
4-31 G	−918.647540	−918.591285[b]	35.30	930.3	37.96
4-31 G(**)	−918.649382	−918.604737	28.02	918.9	30.65
4-31 G**	−918.687646	−918.645779	26.27	869.6	28.76
[6s5p](**)	−919.674645	−919.644168	19.13	910.9	21.73
[6s5p]**	−919.684183	−919.654063	18.90	885.8	21.43
[6s5p](**)+diff	−919.677933	−919.650648	17.12	943.2	19.82
[6s5p]**+diff	−919.687388	−919.660463	16.90	848.9	19.33

a) Total energy at R_{Cl-H} = 2.4087 a.u. and R_{H-Cl^-} = 400 a.u. b) Total energy at R_{Cl-H} = 2.4087 a.u. and R_{H-Cl^-} = 20 a.u.

TABLE 4. CALCULATED HYDROGEN BOND ENERGY OF HCl_2^- (CI CALCULATION)
(1 kcal mol^{-1}=4.184× 10^3 J mol^{-1})

Basis set[a]		E_{min} / hartree	E_{400}[b] / hartree	ΔE / kcal mol^{-1}	Vibrational correction / cm^{-1}	ΔE_{corr} / kcal mol^{-1}
4-31 G	(3321)	−918.746132	−918.695165[c]	31.98	865.0	34.45
4-31 G(**)	(3321)	−918.752865	−918.707077	28.73	1002	31.59
	(5565)	−918.759847	−918.714882	28.22	960.1	30.97
4-31 G**	(4005)	−918.828444	−918.785176	27.15	508.1	28.60
	(13041)	−918.965735	−918.917897	30.02	897.3	32.59
[6s5p](**)	(5565)	−919.763769	−919.731633	20.17	786.8	22.42
[6s5p](**)+diff	(5565)	−919.738943	−919.702381	22.94	860.4	25.40

a) Numbers in parentheses denote CI matrix expansion. b) E_{400} denotes the total energy at R_{Cl-H} = 2.4087 a.u. and R_{H-Cl^-} = 400 a.u. c) The total energy at R_{Cl-H} = 2.4087 a.u. and R_{H-Cl^-} = 20 a.u.

ν_3 value for 4-31G(**) SDQ is 711.5 cm^{-1} and for 4-31G** SDQ (2) is 1094 cm^{-1}. Since SCF results for [6s5p](**), [6s5p]**, and [6s5p]**+diff give the counterpart of 4-31G** SCF results, 4-31G** represents the large basis sets. The shift of basis sets from 4-31G(**) to 4-31G** may represents the change from double minima to single minimum in the large CI and SDQ calculations. The experimental values of isotope frequency ratio ν_3^H/ν_3^D are near the harmonic value 1.42 for $(C_2H_5)_4N^+HCl_2^-$, 1.37 for n-$(C_3H_7)_4N^+HCl_2^-$, and 1.48 for n-$(C_5H_{11})_4N^+$-HCl_2^- in solution. In Table 2 the isotope frequency ratios for $M^+HCl_2^-$ (M=alkali metal) in argon matrix are given and ν_3^H/ν_3^D values vary from 1.42 to 1.51. The calculated results to provide lower ν_3 values (*i.e.* in the case of double minimum potential) show greater ν_3^H/ν_3^D values than the harmonic ones. ν_3^H/ν_3^D values close to harmonic ones are attained in the cases of single minimum potential. Introduction of CI reduces ν_3^H/ν_3^D value to the extent of the decrease of the central barrier in every case, but increase ν_3 value to be greater than 1000 cm^{-1}.

Tables 3 and 4 show the calculated hydrogen bond energies of HCl_2^- for SCF and CI calculations. Vibrationally corrected hydrogen bond energy ΔE_{corr} is obtained as follows;

$$\Delta E_{corr} = (E_{\infty}^{ClHCl^-} - E_{min}^{ClHCl^-}) + (E_{vib}^{HCl} - E_{vib}^{ClHCl^-}), \quad (5)$$

where $E_{\infty}^{ClHCl^-}$ denotes the total engy at $R_{H\cdots Cl}=\infty$ which is replaced by the value at R_{Cl-H}=2.4087 a.u. and $R_{H\cdots Cl}$=400 a.u., $E_{min}^{ClHCl^-}$ denotes the minimum energy in the total potential surface, E_{vib}^{HCl} denotes the vibrational zero point enrgy of HCl molecule and $E_{vib}^{ClHCl^-}$ denotes the vibrational ground state energy of $ClHCl^-$. The former parenthesis in Eq. 5 means the contribution of electronic energy difference between Cl–H···Cl^- and $ClHCl^-$. And the latter means the vibrational correction part. ΔE value is also estimated by the difference between the energies of HCl+Cl^- and $ClHCl^-$ (*i.e.* $\Delta E'=E_{Cl^-+HCl}-E_{min}^{ClHCl^-}$). In the case of 4-31G ΔE become 31.70 kcal mol^{-1} for SCF and 30.96 kcal mol^{-1} for CI, where the number of CI matrix expansion is employed the value 325 for HCl and 153 for Cl^-. Though ΔE values are greater than $\Delta E'$ in the case of 4-31G, we employ the ΔE value for simplicity of the estimation of CI energy. Orbital crossings to make significant change of CI correction value have not occured in every calculation between the equilibrium point and near dissociation limit. We also employed the correction by the experimental value of the vibrational zero point energy of HCl. The experimental vibrational constants of HCl are ω_e=2990.9 cm^{-1} and $\chi_e\omega_e$=52.8 cm^{-1}.[43] Thus the zero point energy of HCl is 1482.3 cm^{-1}. The vibrational correction terms are evaluated by the difference between the zero point energy of free HCl and the sum of zero point energy of ν_1 and ν_3. In comparison with the experimental value of hydrogen bond energy of HCl_2^- (18.9 kcal mol^{-1}), calculated values by 4-31G and its extended basis sets are fairly overestimated both in SCF and CI calculations. Though introduction of polarization functions reduce

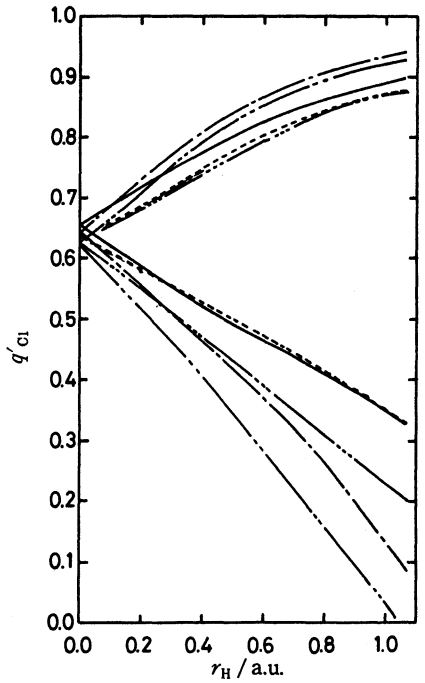

Fig. 5. Shift value of atomic charge on Cl ($q'_{Cl}=q_{Cl}-17.0$) with the proton displacement from the symmetric position at $R_{Cl-Cl}=3.228$ Å for 4-31G, 4-31G(**), and 4-31G**, at $R_{Cl-Cl}=3.157$ Å for [6s5p](**) and at $R_{Cl-Cl}=3.143$ Å for [6s5p]**. ------: 4-31G SCF, -----: 4-31G(**) SCF, ——: 4-31G** SCF, —-—: [6s5p](**) SCF, and ·-·-·: [6s5p]** SCF. CI results are not shown because the shifts on CI from SCF values are not so remarkable.

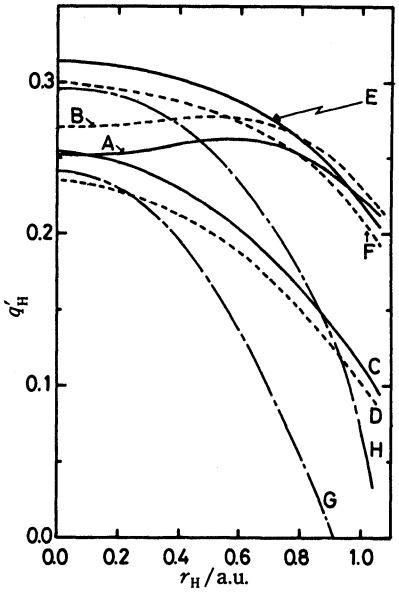

Fig. 6. Shift value of atomic charge on H ($q'_H=1.0-q_H$) with the proton displacement from the symmetric position at $R_{Cl-Cl}=3.228$ Å. R_{Cl-Cl} values are the same as that of Fig. 5. A: 4-31G SCF, B: 4-31G(**) CI (the number of CI matrix expansion is 3321), C: 4-31G(**) SCF, D: 4-31G(**) CI (CI expans.=5565), E: 4-31G** SCF, F: 4-31G** CI (CI expans.=13041), G: [6s5p](**) SCF, and H: [6s5p]** SCF.

both ΔE value and vibrational correction value and then reduce ΔE_{corr}, ΔE is rather greater than the experimental one in the best approximation. CI results are greater than SCF ones except for 4-31G. This is attributed to the difference of the weight of CI estimation in the total energy between $(Cl-H-Cl)^-$ and $Cl-H\cdots Cl^-$. Since SCF energy for 4-31G is obtained at $R_{H\cdots Cl^-}=20$ a.u. by the computational restriction, CI correction value is taken much more than in other cases. The SCF energy difference between the point at $R_{H\cdots Cl^-}=$ 200 a.u. and 400 a.u. is in the order 10^{-6} Hartree which approaches to the threshold of SCF convergence 10^{-7} hartree. The ΔE_{corr} values for [6s5p](**) and its extended basis sets are close to the experimental value. The extension of the basis set reduce the calculated hydrogen bond energy ΔE_{corr}. The effect by diffuse function is greater than that by 3d polarization functions. Though CI increase ΔE_{corr}, the weight of CI is greater in [6s5p](**) than in [6s5p](**)+diff. ΔE_{corr} value (SCF) for [6s5p]**+diff (19.33 kcal mol^{-1}) closes to the experimental one.[14] This is better than the SCF value, 28.96 kcal mol^{-1}, by Thomson *et al.*[14] $\Delta E'$ value for 4-31G SCF, 31.7 kcal mol^{-1}, is in agreement with the result by Alagona.[42] Our results give support to the experimental prediction of hydrogen bond energy of isolated HCl_2^- ion by Ault and Andrews[26] as 18—20 kcal mol^{-1}.

To verify the propriety of the basis sets we also estimated the shift of atomic charge on Cl and H with the proton displacement from the central position in Figs. 5 and 6 respectively. The shifts of atomic charge on Cl indicate no significant variation between SCF and CI, and among small basis set and extended ones. The curve for CI are not shown in Fig. 5. In Fig. 5 it is shown that there is little difference on the charge of Cl^- between the curves for 4-31G and 4-31G**, but significant difference on the charge of Cl at HCl side in the process $ClHCl^- \longrightarrow ClH+Cl^-$. The shift of Cl charge on HCl molecule is the same for 4-31G and 4-31G** and is also the same for [6s5p]** and 4-31G(**). The shift of Cl^- charge is in similar curves for [6s5p]** and [6s5p](**). These results provide the fact that the effect of 3d polarization function appears mainly on the HCl molecule rather than Cl^- and calculated hydrogen bond energy is fairly improved as the difference between the charges on Cl^- and Cl become greater with the extension of basis set. The improvement by the extension of basis sets appears considerably on Cl atom of HCl. Figure 6 shows the shift of atomic charge on H with the proton displacement from the central position. For every basis set SCF and CI curves are nearly in pararrel but slightly close with each other in an asymmetric region. The anomalous variations of q'_H are detected for 4-31G results. 4-31G(**) and [6s5p](**) curves are close to 4-31G curve at $r_H=0$ a.u. and q'_H decrease monotonically in asymmetric region. The reason of the anomalous shift of q'_H is attributed to the lack of 2p polarization functions on H atom. The q'_H values for extended basis sets (*i.e.* 4-31G** and [6s5p]**) are almost the same and are about 0.3 at $r_H=0$ a.u., but the shift along r_H is the greatest for [6s5p]**. The great variations of

q'_H are detected for Dunning basis sets. The shift values for 4-31G and its extended basis sets are rather small. It is summarized that,

(i) the effect of 3d polarization functions on Cl appears to be the increace of q'_H at $r_H=0$ a.u.,

(ii) the effect of 2p polarization functions on H atom reduces the anomalous change of q'_H,

(iii) the effect of basis set extension 4-31G→[6s5p] results in a great shift of q'_H along r_H.

The check on R_{Cl-Cl}, the hydrogen bond energy and (q'_{Cl}, q'_H) indicate that the addition of 2p polarization functions on the basis functions of hydrogen bonding H atom makes remarkable improvement for the calculation and that even in the calculation by small basis set such as 4-31G** the potential function around the equilibrium distance may provide the reliable vibrational constants of HCl_2^-.

Discussion

As mentioned in the previous section, in type II spectra of $ClHCl^-$ anion the experimental values of ν_3 are classified into the two series of data. One is predicted to take the value about 1050 cm^{-1} in $CsCl\cdot 1/3$ [H_3O^+-HCl_2^-] crystal.[23] And another is about 700 cm^{-1} in $M^+HCl_2^-$ (M=alkali metal) in argon matrix.[17,26] One of our results by the use of 4-31G** basis set and CI calculation seems to correspond to the experimental value. However the results by 4-31G(**) and [6s5p](**) seems to correspond to the latter experimental value. Our results of R_{Cl-Cl} by the use of 4-31G** CI correspond to the former experimental one ($R_{Cl-Cl}=3.14$ Å). Whereas the calculated results $R_{Cl-Cl}=3.22$ Å and $\nu_3=700$ cm^{-1} are obtained by the use of 4-31G(**) and [6s5p](**) basis sets. Since the SCF results for [6s5p] system are the counterparts of that for 4-31G system, we discuss only the case of the latter basis set system from now on. The value $\nu_1=257$ cm^{-1} by 4-31G(**) CI calculation is only 3% greater than the experimental value. The value $\nu_3=686.2$ cm^{-1} is also in the same agreement with the average experimental ν_3 value 712 cm^{-1} (4% smaller). The same vibrational constants are predicted by the use of two dimensional analysis[43] of Lippinocott-Schröder potential.[11] By the use of vibrational SCF calculation for two dimensional potential surface, the results $\nu_3^H=652$ cm^{-1} and $\nu_3^D=459$ cm^{-1} ($\nu_3^H/\nu_3^D=1.42$) are obtained.[44] Whereas the prediction of ν_3 by one dimensional vibrational analysis results in $\nu_3^H=762$ cm^{-1} and $\nu_3^D=455$ cm^{-1} ($\nu_3^H/\nu_3^D=1.67$).[11] That is, the vibrational interaction between ν_1 and ν_3 makes the harmonic value of isotope frequency ratio. But these will be a fortuitious results. The results by larger basis sets including 3d polarization functions on Cl atoms predict the larger vibrational frequencies and shorter R_{Cl-Cl} distance The value $\nu_1=352$ cm^{-1} by 4-31G** CI(2) calculation is 41% greater than the experimental values except for $Na^+HCl_2^-$, but is only 17% over estimation for $Na^+HCl_2^-$. If the calculated ν_3 value 1050 cm^{-1} is overestimated, the predicted ν_3 value by the same correction (41% or 17%) comes to be 620 cm^{-1} or 872 cm^{-1}. It is possible to predict that ν_3 value in type II salt is about 700 cm^{-1}. In comparison with the experimental ν_3 value for $CsCl\cdot 1/3$ [$H_3O^+HCl_2^-$] is 1050—1200 cm^{-1}, calculated value 1050 cm^{-1} is in underestimation, which is the same in the case of 4-31G(**). It is also possible to predict that the shorter hydrogen bond ($R_{Cl-Cl}=3.14$ Å) may have the ν_3 value about 1050 cm^{-1} and have a single minimum potential. Since Schröder have not obtained the IR spectra for $CsCl\cdot 1/3$ [$H_3O^+DCl_2^-$], we can not clarify which of the ν_3 values are reasonable from the view point of isotope effect. At least we can predict that HCl_2^- anion in the shorter R_{Cl-Cl} distance ($R_{Cl-Cl}=3.14$ Å) has a single minimum potential and that the symmetric HCl_2^- anion causes the type II spectra which is perfectly different from type I in smaller ν_3 value.

We have not calculated the potential surface of ν_2 mode. From the group theory consideration in centrosymmetric HCl_2^- anion ($D_{\infty h}$ symmetry) ν_1, ν_2, and ν_3 modes have the symmetry species $\sum_g^+$, Π_u, and $\sum_u^+$ respectively.[18] This implies that the inter-mode interaction is negligible between ν_2 and ν_3 and between ν_1 and ν_3. Experimentally ν_1 and ν_2 values indicate no significant shifts between type I and type II salts in comparison with the great shift of ν_3. Thus we concern mainly with the one dimesional potential surface along the D_∞ axis for the ion.

^{35}Cl Nuclear Quadrupole Resonance (NQR) spectroscopy provides the information about the position of H atom in HCl_2^- ion, *i.e.* whether the ion is centrosymmetric or not. Type I salts indicate ^{35}Cl NQR value near 20 MHz, *i.e.* 20.22 MHz for $(CH_3)_4N^+HCl_2^-$ (at 77 K),[24,45,46] 21.27 MHz for $Cs^+HCl_2^-$ (at 166 K).[24] Whereas type II show the value about 12 MHz, *i.e.* 11.89 MHz[24] or 12.48 MHz[47] for $(C_2H_5)_4N^+HCl_2^-$ (at 77K), 11.94 MHz for $CsCl\cdot 1/3$ [$H_3O^+HCl_2^-$] (at 203 K).[24] Townes-Dailey theory relates the ^{35}Cl quadrupole coupling constant e^2qQ/h with the charge δ_{Cl} on Cl by the following formula,

$$(e^2qQ/h)_{ion}(e^2qQ/h)_{atom} = 1 - \delta_{Cl}, \quad (6)$$

where δ_{Cl} is corresponding to q'_{Cl} in Fig. 5. Using this relation and the experimental NQR data, Evans and Lo estimated the net-charge density distribution of symmetric HCl_2^- anion.[47] The results are Cl(0.86)··· H(0.57)–Cl(0.57) for asymmetric anion and Cl(0.74)–H(0.52)–Cl(0.74) for symmetric one. This suggests that the large ^{35}Cl NQR frequency is attributed to the small net-charge density of Cl atom on HCl side of asymmetric ion and the low frequency to the relatively high density of the symmetric one. This picture is supported by Cousseau *et al.* (1973) on the same estimation for $[(C_2H_5)_3NH]^+HCl_2^-$ salt.[48] A priori accurate theoretical prediction of ^{35}Cl NQR frequency on HCl_2^- ion is given by Thomson *et al.*[14] ^{35}Cl NQR value by the use of Townes-Dailey theory and MO calculation is 21.0 and 6.3 MHz for asymmetric ion ($R_{Cl-Cl}=3.22$ Å and $R_{HCl}=1.365$ Å), 13.11 MHz for symmetric ion ($R_{Cl-Cl}=3.14$ Å and $R_{HCl}=1.57$ Å). We have the net charge distribution on HCl_2^- ion for the variation of basis set and the method (SCF and CI). (See Figs. 5 and 6.) From Fig. 5 we can see that the charge distribution on Cl split into Cl^- and Cl in HCl molecule with the variation of H position. The q'_{Cl} value at the symmetric

position is estimated about 0.62—0.65 which is in somewhat underestimation with the result by Evans and Lo.[47] In the asymmetric position of proton our result by 4-31G(**) predicts q'_{Cl} values as 0.52 and 0.70 (at r_H= 0.228 Å), which are in well agreements with the results by Evans and Lo.[47] The tendencies are same in larger basis sets. There are some discussions on the reliability of Mulliken population analysis.[51] But we can explain qualitatively the shift of charge density according to the equilibrium position of proton. These gross population on atoms are not so unrealistic. Cousseau *et al.* (1973)[49] also discussed the proton NMR shift on HCl_2^- ion. The proton NMR chemical shift values are 9.6 ppm for asymmetric ion and 13.9 ppm for symmetric ion. Martin and Fujiwara (1971)[50] suggested that in these cylindrically symmetric system all the significant contributions to the ^1H shielding increasing 1s orbital population of H atom. Estimated δ_H values by Cousseau *et al.* are 0.50 for asymmetric and 0.42 for symmetric ion. Thus the large ^1H shift is the corresponding with the low density on H atom of symmetric HCl_2^- ion. Figure 6 shows that our results on δ_H at symmetric position are scattered in region from 0.77 to 0.69, where δ_H is corresponding to $1.0-q'_H$ in Fig. 6. The result by 4-31G** SCF is 0.69 (at symmetric position). This result is relatively great in comparison with the results by Evans and Lo[47] and Cousseau *et al.*[49] But we can see from Fig. 6 that the increacing tendency of δ_H from the symmetric to asymmetric position seems to explain the difference of ^1H chemical shift between the symmetric position and the asymmetric position of H atom. The relatively low net-charge density on H atom is also explained by the spacing of MO in the occupied valence and virtual regions. Figures 7 and 8 show the orbital correlation diagrams of HCl_2^- ion for 4-31G(**) and 4-31G** basis sets. Both in HCl and HCl_2^- 1s orbital of hydrogen forms the LUMO and the orbital energy of LUMO is increasing in HCl_2^- in comparison with isolated HCl molecule. Whereas HOMO consists of σ_u orbital which is accompanied by the degenerate orbitals π_g and π_u with the slightly small energy differences. This is due to the long Cl—Cl distance which decrease the in phase overlapping of orbitals and minimize the out of phase overlapping. Then the anti-bonding orbitals σ_u and π_g become stable. As a result 1s orbital of H comes to be LUMO to decrease δ_H and σ_u become HOMO to increase the absolute value of δ_{Cl}. Estimated net-charge density of HCl (literature value) is H(0.62)–Cl(0.38), which turned out to be an opposite net-charge distribution both in symmetric and asymmetric HCl_2^- ions.[47] It is the same in our case that H(0.85)–Cl(0.15) turns out to be Cl(0.63)–H(0.74)–Cl(0.63) for 4-31G(**) SCF. Martin and Fujiwara note that, "As the halide ion, X^-, approaches the positive (H) region of the HX molecule, electronic charge is repelled out of the hydrogen orbital." The situation is well established not only by the shift of q'_{Cl} and q'_H (Figs. 5 and 6) but also by the orbital correlation diagram of HCl_2^- (Figs. 7 and 8).

Figure 8 also explains the anomalous CI potential surface of proton by 4-31G** CI(1) (*i.e.* CI expansion terms are 4005). CI correction energy is abnormally minimized at the center of HCl_2^-. CSF of CI(1) is

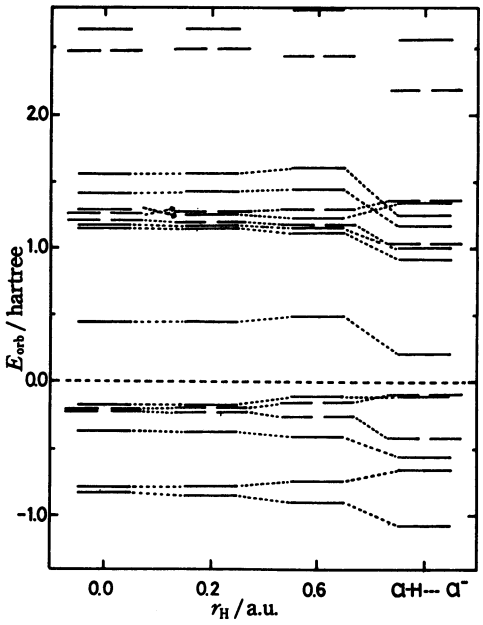

Fig. 7. Orbital correlation diagram of HCl_2^-(4-31G(**) basis set) on the proton displacement from the central position at R_{Cl-H}=3.228 Å. Cl–H···Cl⁻ denotes the position at r_{H-Cl}=1.257 Å and $r_{H\cdots Cl^-}$=211.7 Å, which corresponds to the dissociation limit. Only the orbitals numbered 10—18 (occupied) and 19—31 (unoccupied) are shown. Correlation among the polarization functions are not shown.

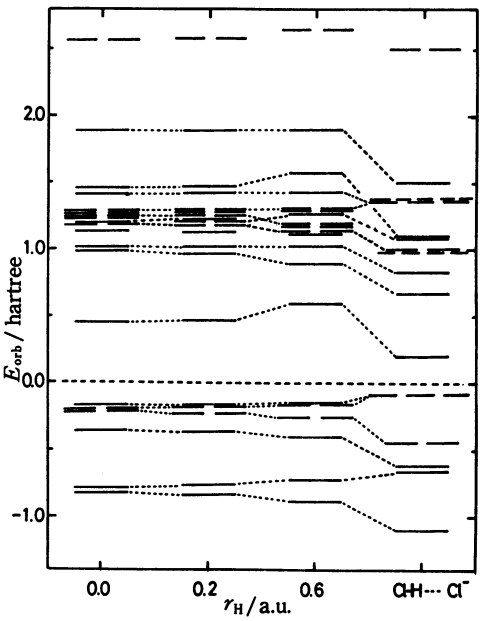

Fig. 8. Orbital correlation diagram of HCl_2^- (4-31G** basis set) on the proton displacement from the central position at R_{Cl-Cl}=3.140 Å. Cl–H···Cl⁻ denotes the position r_{H-Cl}=1.275 Å and $r_{H\cdots Cl^-}$=211.7 Å, which corresponds to the dissociation limit. Only the orbitals numbered 10—18 (occupied) and 19—38 (unoccupied) are shown. Correlation among the polarization functions are not shown.

constructed by the higher 8 occupied valence orbitals and lower 11 unoccupied orbitals. From Fig. 8 we can see eight doubly degenerate orbitals from 26th to 31st orbital, which correspond to 3d orbitals of Cl atoms. Since the crossing occurs between the lowest degenerate 3d orbitals (26th and 27th orbitals) and the 25th orbital in a region 0 a.u.$<r_H<$0.2 a.u., the contributions to the CI correction energy from these orbitals indicate significant change. Since CSF of CI(2) (CI expansion terms are 13041) consists of 8 occupied orbitals and 20 virtual orbitals, the anomalous potential surface is not formed. Though 4-31G$^{(**)}$ orbital correlation diagram (Fig. 7) indicates such crossings among the orbitals 24th, 25th (degenerate), and 26th, CSF consists of 8 occupied orbitals and 10 (CI expansion terms are 3321) or 13 (CI expansion terms are 5565) virtual orbitals. Thus the anomalous proton potential surface is not formed by any CI calculation for 4-31 G$^{(**)}$ basis set.

Now we have arrived at the conclusion summarized as follows:

(i) Symmetric HCl_2^- ions are formed in the salts which indicate ν_3 mode classified into type II IR spectra. But there is the possibility that the type II salts are classfied into the two types of molecules; *i. e.* one is the salts which indicate $\nu_3=700$ cm^{-1} (*e.g.* $(C_2H_5)_4N^+HCl_2^-$ in aprotic solution or $Rb^+HCl_2^-$ in argon matrix), and another is the salts which possibly indicate $\nu_3=1050$ cm^{-1} and has a single minimum potential of proton and the hydrogen bond length 3.14 Å (*e.g.* CsCl·1/3 [H_3O^+-HCl_2^-] in crystalline state).

(ii) At least we can predict by the largest CI calculation that the isolated linear symmetric HCl_2^- ion has the value $R_{Cl-Cl}=3.14$ Å and single minimum potential which causes the harmonic value of isotope frequency ratio. The SCF calculation by the largest basis set supports this prediction. (*i.e.* SCF barrier is very low and CI reduces the central barrier.) But we can hardly clarify which ν_3 values represents that of the linear symmetric HCl_2^- ion by the lack of accuracy of calculated potential curvature.

(iii) Calculated net-charge distribution also supports the conclusion (i)—(ii) in self consistent standpoint with the ^{35}Cl NQR spectra and ^{1}H NMR spectra which distinguish type II salts from type I salts. But the realistic structures of the former type II salts are not known. Thus we conclude with some reserve that type II HCl_2^- anion has symmetric structure of $D_{\infty h}$ symmetry.

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