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Submillimeter-Wave Spectra of H_2Cl^+ and its Isotopic Species: Molecular Structure

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The rotational spectra of $HD^{35}Cl^+$, $H_2{}^{35}Cl^+$, and $H_2{}^{37}Cl^+$ were measured in the frequency region of 180 to 550 GHz with a source-modulated submillimeter-wave spectrometer. The ions were generated in a free space absorption cell by a hollow-cathode discharge in a gas mixture of Cl_2 and He to which H_2 and/or D_2 was added. Precise molecular constants including the electric quadrupole coupling constants were determined for the three species. The zero-point average structure, r_z, was calculated from moments of inertia corrected for harmonic terms. The harmonic force field of H_2Cl^+ was derived from previously estimated harmonic vibrational frequencies and inertial defects. The r_z structures obtained are

$$r_z(\text{Cl–H}) = 1.320\,57(48)\ \text{Å} \quad \text{and} \quad \theta_z(\text{H–Cl–H}) = 94.238(72)^\circ \text{ for } H_2{}^{35}Cl^+$$

and

$$r_z(\text{Cl–H}) = 1.320\,60(38)\ \text{Å} \quad \text{and} \quad \theta_z(\text{H–Cl–H}) = 94.239(58)^\circ \text{ for } H_2{}^{37}Cl^+,$$

where values in parentheses indicate errors due to residual inertial defects among the corrected moments of inertia. When the θ_z of $HD^{35}Cl^+$ is assumed to be the same as that of $H_2{}^{35}Cl^+$, the r_z(Cl–H) and r_z(Cl–D) lengths of $HD^{35}Cl^+$ are calculated to be 1.320 69(69) Å and 1.316 54(111) Å, respectively.

INTRODUCTION

The most valuable information obtained from high-resolution spectroscopy is precise structure determination, which has led to the elucidation of the structure of many basic stable molecules and free radicals. The precise structure determination of molecular ions is not straightforward because measurements of several isotopic species or force field analyses are needed for chemically active and short-lived polyatomic molecular ions. Only a limited number of molecular ions have been subjected to such intensive structure-determination studies.

The protonated hydrogen chloride ion, H_2Cl^+, is one of the fundamental triatomic molecular ions. The first structural information on this ion was reported in 1986 by Kawaguchi and Hirota (*1*), who studied its ν_2 band with infrared diode laser spectroscopy and derived the r_0 structure from observed rotational constants. Based on this infrared study, Saito *et al.* (*2*) detected microwave spectral lines of $H_2{}^{35}Cl^+$ in 1988 and determined the rotational constants of the ground state more precisely. In the same year Lee *et al.* (*3*) examined the ν_1 and ν_3 bands using difference frequency laser spectroscopy. Detailed knowledge of the changes of rotational constants by excitation of each mode led them to determine the r_e structure of H_2Cl^+. Several quantum chemical calculations (*4–7*) were performed to predict various physical properties of H_2Cl^+. Botschwina (*7*) carried out an extensive CEPA-1 (coupled electron-pair approximation) calculation and predicted equilibrium geometry and harmonic and anharmonic vibrational frequencies adjusted to observed fundamentals. Some discussions were devoted to its interstellar existence (*8–10*), but no detection of H_2Cl^+ in space has been reported so far, though HCl, which is a main product of the dissociative recombination of H_2Cl^+, was identified toward OMC-1 (*11*).

H_2Cl^+ is a light molecule. Saito *et al.* (*2*) measured only four rotational transitions of the ground state below 400 GHz, which were used to determine three rotational constants and one of the quartic centrifugal distortion constants, Δ_{JK}. When one of the hydrogens is replaced by a deuterium atom, the principal inertial axis rotates by 35.4° and $HDCl^+$ has a μ_a dipole component of $0.579\mu_b$, where μ_b is the dipole moment of the symmetric H_2Cl^+. Therefore, $HDCl^+$ has *a*-type transitions with half the intensity of *b*-type transitions and gives more observable transitions in the submillimeter-wave region. From these transitions detailed and precise molecular constants can be determined.

In the present study we measured *a*- and *b*-type rotational spectral lines of $HD^{35}Cl^+$ and several lines of $H_2{}^{35}Cl^+$ and $H_2{}^{37}Cl^+$ with submillimeter-wave spectroscopy. The precise rotational constants determined were used to discuss the molecular structure of H_2Cl^+.

EXPERIMENTAL

The submillimeter-wave spectrometer previously reported (*12*) was used to measure spectral lines of the ions. The monodeuterated species, $HD^{35}Cl^+$, was produced by a hollow cathode discharge in a Pyrex-glass free-space absorption cell 2 m in length and 10 cm in diameter. The cathode employed was a 1.1-m stainless-steel tube. A known spectral line of $H_2{}^{35}Cl^+$ (2) was used to optimize its production conditions: the discharge current was 400 mA, and partial pressures were 3 mTorr of Cl_2, 3 mTorr of H_2, 3 mTorr of D_2, and 10–20 mTorr of He. The cell temperature was maintained at −90 to −120°C.

Prior to observations of $HD^{35}Cl^+$ spectral lines, transition frequencies of $HD^{35}Cl^+$ were calculated from rotational constants which were derived from an r_0 structure (1). As discussed above, the $HDCl^+$ ion has both *a*- and *b*-type rotational transitions. A relatively strong *b*-type transition, 3_{12}–3_{03}, was initially searched for in the 380–390 GHz region. This wide frequency region of about 10 GHz was due to an unknown inertial defect of the $HD^{35}Cl^+$ species. A quartet of lines was detected at 383.2 GHz and found to show the same behavior as the spectral lines of $H_2{}^{35}Cl^+$. The line intensities decreased to one-half by application of an external magnetic field of 30 G. The quartet lines also showed an intensity dependency on change of partial pressures of both H_2 and D_2. The above behavior and production chemistry suggested that the quartet lines originated from a molecular ion bearing H and D atoms. The quartet structure was consistent with a hyperfine structure due to a nuclear quadrupole interaction of $I = 3/2$. As noted above, the principal axis of $H_2{}^{35}Cl^+$ rotates by 35.4° on a single deuteration, which also rotates the axis of the electric quadrupole coupling tensor for ^{35}Cl by the same magnitude. This gives a hyperfine structure for the 3_{12}–3_{03} transition compatible to the observed quartet lines. Similarly, *a*-type transitions were identified. No further splittings due to the deuterium nucleus were observed because of the relatively large linewidths of the ion. In total, 12 rotational transitions including 9 *b*-type and 3 *a*-type transitions were measured as listed in Table 1.

Furthermore, three transitions of the $H_2{}^{35}Cl^+$ species and seven of $H_2{}^{37}Cl^+$ were newly measured and are listed in Tables 2 and 3 respectively. Figure 1 shows the 4_{31}–4_{22} transition of $H_2{}^{37}Cl^+$, representing a typical observed signal-to-noise ratio and an example of the quartet hyperfine structure.

The observed line frequency is Doppler shifted by ion-drift velocity. The magnitude of the shift depends on the discharge conditions. It was estimated from a difference between the observed frequencies of a relatively strong line at 380 GHz, the 3_{21}–3_{12} transition of $H_2{}^{35}Cl^+$, with normal and opposite electrode configurations, where radiation passed from the anode to the cathode in the normal configuration and vice versa in the opposite configuration. The difference between measured frequencies with both configurations was 0.174(35) MHz, where the value in parentheses is one standard error of the measurements. This shift was used to correct the measured frequencies of all the observed lines with a proportionality factor of $2.3 \times 10^{-7}\,\nu$ MHz, where ν is the line frequency. Corrected line frequencies are listed in Tables 1 to 3. Several lines of $H_2{}^{35}Cl^+$

TABLE 1

Observed and Calculated Transition Frequencies of $HD^{35}Cl^+$ (in MHz)

$J'_{K_a'K_c'}$–$J_{K_aK_c}$	F'–F	$\nu_{\text{obs.}}$[a]	$\Delta\nu_{\text{obs.–calc.}}$[b]
b-type			
1_{10}–1_{01}	0.5–1.5	208 531.477(19)	−0.039
	2.5–2.5	208 535.358(20)	0.194[c]
	1.5–0.5	208 544.725(13)	0.326[c]
	2.5–1.5	208 545.979(26)	0.426[c]
	1.5–2.5	208 552.733(18)	0.022
2_{11}–2_{02}	0.5–0.5	271 637.268(14)	0.017
	1.5–0.5	271 644.456(21)	−0.001
	3.5–3.5	271 652.069(6)	−0.042
	1.5–1.5	271 657.963(24)	0.005
	2.5–1.5	271 663.144(16)	−0.020
	1.5–2.5	271 667.569(7)	0.074
	2.5–2.5	271 672.722(21)	0.011
2_{02}–1_{11}	2.5–2.5	340 585.234(45)	0.077
	2.5–1.5	340 592.538(28)	0.029
	3.5–2.5	340 598.942(28)	−0.118[c]
	1.5–1.5	340 602.407(31)	−0.030[d]
	0.5–0.5		
3_{12}–3_{03}	1.5–1.5	383 190.647(11)	0.004
	4.5–4.5	383 200.250(26)	−0.127[c]
	2.5–2.5	383 211.288(10)	−0.214[c]
	3.5–3.5	383 221.213(15)	−0.024
1_{11}–0_{00}	1.5–1.5	410 286.373(26)	0.015
	2.5–1.5	410 293.588(29)	0.073
	0.5–1.5	410 299.209(48)	−0.032
3_{21}–3_{12}	1.5–1.5	449 729.024(14)	−0.297[c]
	4.5–4.5	449 731.067(13)	0.026
	2.5–2.5	449 733.028(28)	0.022
	3.5–3.5	449 734.691(10)	−0.035
4_{22}–4_{13}	2.5–2.5	452 170.198(18)	−0.352[c]
	5.5–5.5	452 172.444(12)	−0.025
	3.5–3.5	452 175.789(30)	−0.234[c]
	4.5–4.5	452 177.965(12)	0.024
2_{20}–2_{11}	3.5–3.5	479 651.332(40)	−0.011
	2.5–2.5	479 657.480(142)	−0.219[c]
4_{13}–4_{04}	2.5–2.5	549 757.188(58)	−0.021
	5.5–5.5	549 764.745(43)	0.017
	3.5–3.5	549 778.664(77)	0.011
	4.5–4.5	549 786.175(37)	0.003
a-type			
1_{01}–0_{00}	1.5–1.5	253 984.440(29)	−0.051
	2.5–1.5	253 994.875(27)	−0.005
3_{12}–3_{13}	4.5–4.5	311 720.429(24)	0.030
	2.5–2.5	311 733.388(29)	−0.022
	3.5–3.5	311 744.765(12)	−0.029
2_{12}–1_{11}	2.5–1.5	455 570.414(27)	−0.026[d]
	1.5–0.5		
	3.5–2.5	455 580.884(27)	−0.044[c]

[a] Ion-drift Doppler shifts were corrected. Values in parentheses indicate one standard deviation of the frequency measurements and apply to the last digits of the constants.

[b] Residuals in the least-squares fit: $\Delta\nu = \nu_{\text{obs.}} - \nu_{\text{calc.}}$

[c] Not included in the least-squares fit.

[d] Blend of two lines. The calculated frequency is obtained by averaging component frequencies weighted in proportion to their relative intensities.

TABLE 2

Observed and Calculated Transition Frequencies of $H_2{}^{35}Cl^+$ (in MHz)

$J'_{K_a'K_c'}-J_{K_aK_c}$	$F'-F$	$\nu_{\mathrm{obs.}}{}^{a}$	$\Delta\nu^{b}$
$1_{10}-1_{01}$	0.5–0.5	189 200.369(31)	−0.020
	0.5–1.5	189 225.010(10)	0.086^{c}
	2.5–2.5		
	1.5–0.5	189 231.910(27)	0.032
	2.5–1.5	189 238.598(12)	0.112^{d}
	1.5–2.5	189 242.471(10)	-0.119^{d}
	1.5–1.5	189 255.994(27)	0.014
$2_{20}-2_{11}{}^{e}$	0.5–1.5	271 263.958(33)	-0.151^{d}
	0.5–0.5	271 268.233(46)	0.020
	3.5–2.5	271 274.365(38)	0.129^{d}
	3.5–3.5	271 278.240(25)	−0.100
	1.5–1.5	271 282.352(25)	−0.039
	1.5–0.5	271 286.536(29)	0.041
	2.5–2.5	271 292.508(31)	-0.010^{d}
$3_{21}-3_{12}$	1.5–1.5	380 097.119(11)	-0.229^{d}
	4.5–4.5	380 102.338(16)	0.046
	4.5–3.5	380 104.455(20)	0.328^{d}
	2.5–1.5	380 106.089(38)	−0.020
	2.5–2.5	380 108.137(24)	0.193^{d}
	3.5–3.5	380 112.912(17)	0.023
$2_{11}-2_{02}{}^{e}$	3.5–3.5	395 076.559(25)	−0.025
	2.5–2.5	395 098.946(41)	−0.025
$3_{30}-3_{21}$	1.5–1.5	417 225.432(22)	0.073
	4.5–4.5	417 230.213(12)	−0.077
	2.5–2.5	417 235.982(10)	0.056
	3.5–3.5	417 240.831(20)	−0.027
$4_{31}-4_{22}$	2.5–2.5	420 551.310(15)	-0.148^{d}
	5.5–5.5	420 553.809(9)	−0.001
	3.5–3.5	420 558.097(14)	−0.070
	4.5–4.5	420 560.576(9)	0.056
$1_{11}-0_{00}{}^{c}$	1.5–1.5	485 413.427(29)	−0.040
	2.5–1.5	485 417.670(15)	0.099
	0.5–1.5	485 420.796(57)	−0.059

[a] Ion-drift Doppler shifts were corrected. Values in parentheses indicate one standard deviation of the frequency measurements and apply to the last digits of the constants.

[b] Residuals in the least-squares fit: $\Delta\nu = \nu_{\mathrm{obs.}} - \nu_{\mathrm{calc.}}$

[c] Blend of two lines. The calculated frequency is obtained by averaging component frequencies weighted in proportion to their relative intensities.

[d] Not included in the least-squares fit.

[e] Reported in Ref. (2). Ion-drift Doppler shifts were corrected.

measured in the previous study (*2*) were corrected with the same factor, because spectrometer configurations of absorption cells and experimental conditions employed at Nagoya University (*13*) and by the present study (*12*) were almost the same.

The measured spectral line frequencies were analyzed using a conventional Hamiltonian for an asymmetric top molecule with chlorine nuclear quadrupole interaction. All $\Delta J = \pm 1$, ± 2 matrix elements were included in the analysis, where the energy levels were calculated by direct numerical diagonalization of Hamiltonian matrices and molecular parameters were determined by the least-squares method fitting the observed line frequencies (*2*).

Forty-six lines of $HD^{35}Cl^+$ were analyzed to determine three rotational constants, five quartic centrifugal distortion terms, one sextic distortion term, and two electric quadrupole coupling constants. A nonaxial component of the quadrupole coupling tensor of about 18.5 MHz was expected to be due to the principal axis rotation from the parent species to the deuteride species, but its effect on transition frequency was too small and χ_{ab} was not determined experimentally. For the $H_2{}^{35}Cl^+$ and $H_2{}^{37}Cl^+$ species seven rotational transitions were observed, which led to the determination of three rotational constants and three quartic centrifugal distortion constants. In order to obtain good fittings in these cases, it was necessary to use the known sextic centrifugal distortion constants (*3*). Furthermore, it turned out that a good fitting was not obtained for the $H_2{}^{37}Cl^+$ species with the sextic distortion terms by Lee *et al.* (*3*). Therefore, the sextic terms for the $H_2{}^{35}Cl^+$ species were used instead in the analysis of the $H_2{}^{37}Cl^+$ spectral lines.

TABLE 3

Observed and Calculated Transition Frequencies of $H_2{}^{37}Cl^+$ (in MHz)

$J'_{K_a'K_c'}-J_{K_aK_c}$	$F'-F$	$\nu_{\mathrm{obs.}}{}^{a}$	$\Delta\nu^{b}$
$1_{10}-1_{01}$	0.5–1.5	188 428.132(22)	-0.020^{c}
	2.5–2.5		
	1.5–0.5	188 433.716(42)	−0.076
	2.5–1.5	188 438.900(32)	−0.027
	1.5–2.5	188 441.923(19)	-0.362^{d}
$2_{20}-2_{11}$	3.5–3.5	268 962.409(14)	0.002
	2.5–2.5	268 973.719(24)	0.095
$3_{21}-3_{12}$	1.5–1.5	379 497.316(29)	0.174^{d}
	4.5–4.5	379 501.107(14)	0.011
	2.5–2.5	379 505.625(16)	0.010
	3.5–3.5	379 509.494(20)	−0.075
$2_{11}-2_{02}$	3.5–3.5	395 126.135(34)	0.039
	2.5–2.5	395 144.044(58)	0.016
$3_{30}-3_{21}$	1.5–1.5	412 185.007(13)	0.065
	4.5–4.5	412 188.754(8)	−0.068
	2.5–2.5	412 193.238(28)	−0.018
	3.5–3.5	412 197.129(27)	−0.006
$4_{31}-4_{22}$	2.5–2.5	417 888.941(20)	-0.563^{d}
	5.5–5.5	417 891.408(26)	0.035
	3.5–3.5	417 894.481(28)	-0.353^{d}
	4.5–4.5	417 896.685(29)	−0.019
$1_{11}-0_{00}$	1.5–1.5	484 228.484(18)	−0.013
	2.5–1.5	484 231.804(26)	−0.051
	0.5–1.5	484 234.604(25)	0.064

[a] Ion-drift Doppler shifts were corrected. Values in parentheses indicate one standard deviation of the frequency measurements and apply to the last digits of the constants.

[b] Residuals in the least-squares fit: $\Delta\nu = \nu_{\mathrm{obs.}} - \nu_{\mathrm{calc.}}$

[c] Blend of two lines. The calculated frequency is obtained by averaging component frequencies weighted in proportion to their relative intensities.

[d] Not included in the least-squares fit.

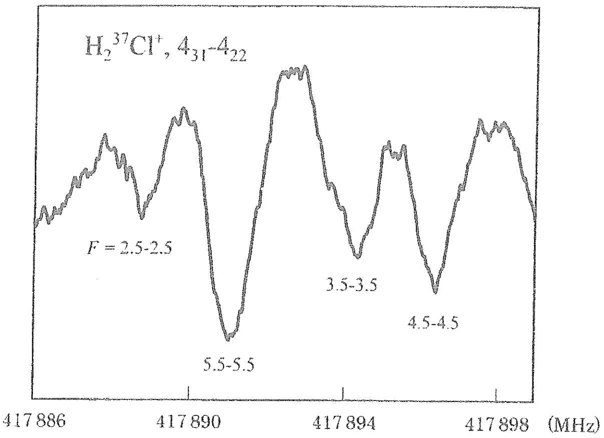

FIG. 1. The hyperfine structure of the 4_{31}–4_{22} transition of $H_2{}^{37}Cl^+$. The ion was produced by a 600-mA dc discharge of a mixture of Cl_2(3 mTorr), H_2(6 mTorr), and He(10 mTorr). The integration time was 40 s.

RESULTS AND DISCUSSION

In the present study precise rotational constants were determined for three isotopic species of H_2Cl^+, whereas centrifugal distortion constants were not fully determined because of the limited number of observed rotational transitions. However, the rotational constants were barely affected by uncertainties in the centrifugal distortion terms. This is because only low-J transitions ($J \leq 4$) were employed in the analysis, and is also supported by agreement within a few megahertz between the present rotational constants and those reported by Lee *et al.* (*3*). These rotational constants were used to elucidate the detailed molecular structure of H_2Cl^+.

Harmonic Force Field

The force field analysis is essential for ascertaining a physically significant and precise molecular structure (*14*). As noted above, Botschwina (*7*) adjusted the CEPA-1 calculated fundamentals to those observed and predicted harmonic frequencies. These harmonic frequencies can be used to determine three of four harmonic force field components. The errors in the predicted harmonic frequencies are not clear, but it may be reasonable to assume the effective errors to be about 1 cm^{-1} (*7*). The remaining one component could be derived in several ways. For H_2Cl^+, centrifugal distortion constants are available for the three isotopic species and inertial defects in the vibrationally excited states as well as in the ground state. Among them, differences between the inertial defects in the vibrationally excited states and in the ground state are useful in the determination of the force field because the differences in the inertial defects mainly arise due to Coriolis terms (*15, 16*). Therefore, the harmonic force field was determined in the present study from predicted harmonic frequencies (*7*), and changes of inertial defects by excitation of vibrational modes (*3*). Among the three derived differences of the inertial defects, one difference, namely the $\Delta^{100} - \Delta_0$, where Δ^{100} and Δ_0 are the inertial defects in the $\omega_1 = 1$ state and in the ground state, respectively, was not included in the analysis. The observed value of $\Delta^{100} - \Delta_0$ is 0.003 302 amu Å^2, where this value should be negative in the case of $\omega_1 > \omega_3$. The reason is that $\zeta_{13}^{(c)}$ is nearly equal to zero in the case of $H_2{}^{35}Cl^+$ and the higher order vibration–rotation contribution to the inertial defect is larger than the $\zeta_{13}^{(c)}$ term. The errors of the inertial defect differences were assumed to about 0.005 amu Å^2 and are comparable to differences between observed and calculated inertial defects for similar molecules (*17*). The weight for all the input data was calculated from the inverse square of the experimental errors. Vibrational frequencies, inertial defect differences, and derived Coriolis coupling constants are listed in Table 5. The harmonic force field of H_2Cl^+ was determined by the least-squares method and is listed in Table 6.

Molecular Structure

The force field determined above was used to calculate the r_z structures of the three H_2Cl^+ species using the standard method (*14*). The harmonic contributions to the observed moments of inertia were calculated by the l-matrix method, and then the r_z structure was derived from the corrected moments of inertia. The small residual inertial defects for $H_2{}^{35}Cl^+$ and $H_2{}^{37}Cl^+$, which ranged from one sixteenth to one twentieth of the observed inertial defects, showed that the correction was plausible (see Table 7). Two r_z structural parameters were determined

TABLE 4

Molecular Constants of $HD^{35}Cl^+$, $H_2{}^{35}Cl^+$, and $H_2{}^{37}Cl^+$ (in MHz)[a]

	$HD^{35}Cl^+$	$H_2{}^{35}Cl^+$	$H_2{}^{37}Cl^+$
A	309 475.966(65)	337 351.913(76)	336 359.961(81)
B	153 167.951(80)	273 587.052(98)	273 587.101(102)
C	100 836.799(60)	148 100.369(69)	147 907.000(70)
Δ_J	2.987 1(86)	20.069 0[b]	20.143[b]
Δ_{JK}	29.694 2(178)	−72.084 0(90)	−71.929 8(107)
Δ_K	−5.814 0(173)	132.167[b]	131.564[b]
δ_J	0.986 68(121)	8.993 9(47)	9.008 6(48)
δ_K	20.412(30)	−1.843 3(66)	−1.995 4(74)
Φ_J		0.007 971[b]	0.007 971[b]
Φ_{JK}		−0.047 25[b]	−0.047 25[b]
Φ_{KJ}		0.038 37[b]	0.038 37[b]
Φ_K		0.069 49[b]	0.069 49[b]
ϕ_J		0.003 930[b]	0.003 930[b]
ϕ_{JK}		−0.013 958[b]	−0.013 958[b]
ϕ_K	−0.035 3(54)	0.041 64[b]	0.041 64[b]
χ_{aa}	−41.56(22)	−53.56(25)	−42.46(41)
χ_{bb}	−28.630(167)	−16.42(28)	−13.43(31)
rms	0.040	0.064	0.061

[a] Values in parentheses denote three times the standard deviation and apply to the last digits of the constants.

[b] Lee *et al.* (*3*).

TABLE 5
Harmonic Frequencies, Inertial Defects, and Coriolis Coupling Constants of $H_2{}^{35}Cl^+$

	Obs.	Calc.
$\omega_1/\mathrm{cm}^{-1}$	2756.8^{a}	2 756.8
$\omega_2/\mathrm{cm}^{-1}$	1219.6^{a}	1 219.6
$\omega_3/\mathrm{cm}^{-1}$	2748.8^{a}	2 748.8
Δ^{100}-Δ_0/amu Å^2	$0.003\,302^{b,c}$	−0.000 227
Δ^{010}-Δ_0/amu Å^2	$0.143\,900^{b}$	0.137 679
Δ^{001}-Δ_0/amu Å^2	$-0.011\,695^{b}$	−0.011 796
$(\zeta_{13}^{(c)})^2$		.000 03
$(\zeta_{23}^{(c)})^2$		.999 97

^{a} Botschwina (*7*).

^{b} Lee *et al.* (*3*).

^{c} Not included in the least-squares fit. See the text.

separately from three averaged moments of inertia for symmetric $H_2{}^{35}Cl^+$ and $H_2{}^{37}Cl^+$. The results are listed in Table 7.

The harmonic corrections to the observed moments of inertia for $HDCl^+$ were calculated similarly by applying the harmonic force field of the symmetric species to that of C_s symmetry. The resulting residual inertial defect is listed in Table 7. The deuterated species has three structural parameters. It is noted that the r_z structural parameters of both symmetric species are almost equal and within their errors. Since the force field of the bending mode is almost harmonic (*18, 19*), the θ_z of $HD^{35}Cl^+$ is safely assumed to be the same as that of the $H_2{}^{35}Cl^+$. The r_z bond lengths of $HD^{35}Cl^+$ were calculated from the corrected moments of inertia using the least-squares method and the weight was assumed to be proportional to the magnitude of Jacobians against θ. Thus, two bond lengths of $HD^{35}Cl^+$ were determined separately and listed in Table 8. The r_z(Cl–D) length is found to differ from r_z(Cl–H) by 0.004 2(18) Å, which is of a magnitude similar to that of other simple hydrogen-bearing molecules (*18, 20*) and is brought about by anharmonicity of the bond concerned (*21*). When this difference is applied to the diatomic approximation (*22*), the r_e(Cl–H) length is estimated from the bond lengths r_z(Cl–H) and r_z(Cl–D) to be r_e(Cl–H) = 1.306 0(57) Å, which agrees well with r_e(Cl–H) = 1.304 12(17) Å as reported by Lee *et al.* (*3*), though the error of the present result is larger than that reported by Lee *et al.* The r_z(Cl–H) of $HD^{35}Cl^+$ differs from that of $H_2{}^{35}Cl^+$ by 0.001 Å, which is marginally within the errors.

TABLE 6
Harmonic Force Field of H_2Cl^+ (in md/Å)^{a}

F_{11}	4.398 8(47)
F_{12}	0.10(24)
F_{22}	0.430 4(103)
F_{33}	4.351 9(39)

^{a} The internal symmetry coordinates: $S_1 = (\Delta r_1(\text{Cl–H}) + \Delta r_2(\text{Cl–H})/\sqrt{2}$. $S_2 = \Delta\theta(\text{H–Cl–H})$. $S_3 = (\Delta r_1(\text{Cl–H}) - \Delta r_2(\text{Cl–H}))/\sqrt{2}$. Numbers in parentheses represent one standard deviation and apply to the last significant digits.

TABLE 7
Inertial Defects and r_z Structure of $H_2{}^{35}Cl^+$, $H_2{}^{37}Cl^+$, and $HD^{35}Cl^+$

	$H_2{}^{35}Cl^+$	$H_2{}^{37}Cl^+$	$HD^{35}Cl^+$
Δ_0	0.067 099	0.067 143	0.079 327
Δ_z	0.004 256	0.003 426	0.007 236
r_z(H–Cl) (Å)	1.320 57(48)	1.320 60(38)	1.320 69(69)^{a}
r_z(D–Cl) (Å)			1.316 54(111)^{a}
θ_z (°)	94.238(72)	94.239(58)	94.238^{b}

^{a} Value in parentheses represent one standard deviation and apply to the last digits of the constants.

^{b} Fixed to the θ_z value of $H_2{}^{35}Cl^+$.

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