

Molecular complexes of water and hydrogen chloride in the atmosphere

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We present a study of structurally nonrigid molecular complexes formed by water and hydrogen chloride molecules being the products of emissions from some chemical and metallurgic plants using theoretical *ab initio* methods. Equilibrium configurations of the complexes $(\text{H}_2\text{O})_n(\text{HCl})_m$ (2:2; 3:3) and positions of vibration bands are determined based on *ab initio* calculations of the potential energy surfaces with application of second-order Möller–Plesset perturbation theory (MP2), split-valence basis set 6-31G (d,p), and correlation-consistent basis set aug-cc-pVDZ. The data obtained are needed for assignment of IR absorption spectra and in real-time remote monitoring of these complexes that are ecologically hazardous under atmospheric conditions.

Introduction

The problem of creation, stability, and optical activity of structurally nonrigid molecular complexes of water with chemically active and toxic molecules of anthropogenic origin is one of the most urgent problems in modern physics and chemistry of the atmosphere. Weakly bound molecular complexes may cause extra radiative losses in the atmosphere. Complexes of hydrogen chloride and water play an important role in the ozone depletion cycle.¹ *Ab initio* investigations of the structure and vibration spectra of weakly bound complexes characterized by several types of large-amplitude motions (LAMs) allow the contribution of these complexes to atmospheric absorption to be assessed. Several types of large-amplitude motions may lead to transformation of vibration spectra of monomers comprising a complex and to the appearance of new bands corresponding to intermolecular vibrations. This opens the possibility for detecting and estimating the concentrations of such complexes in the atmosphere with modern remote laser sensing instrumentation.

A considerable progress has been achieved recently in experimental investigation of intermolecular systems in the gas phase.^{1–15} However, the complete set of intermolecular vibrations is known only for few complexes. The investigators' attention was mostly concentrated at the systems with rather high bond energies, for example, $\text{H}_2\text{O}\dots\text{HF}$ (Ref. 9). Weak hydrogen bonds, such as in $\text{H}_2\text{O}\dots\text{HCl}$, are poorly studied, in spite of their chemical importance. The geometry of this complex was determined by the methods of rotational spectroscopy,¹⁰ but the data on vibrational spectra are limited to intramolecular modes in solid matrices.^{11–14} The geometry of the weakly bound trimer $\text{HCl}(\text{H}_2\text{O})_2$ was found by Kisiel with co-authors¹⁵ from rotational spectra observed at extension of a supersonic jet. The clusters $\text{HCl}(\text{H}_2\text{O})_n$, $n = 1–5$, were studied in Refs. 16 and 17 from the viewpoint of

their stability and protolytic dissociation of the HCl molecule in water clusters. *Ab initio* prediction of rovibrational spectra of $\text{HCl}(\text{H}_2\text{O})_2$ complex with tunneling effects was reported in Ref. 18.

In this paper, we present the results of the quantum-mechanical study of the structure, stability, and vibration spectra of $(\text{H}_2\text{O})_n(\text{HCl})_m$ (2:2, 3:3) complexes.

Calculation methods

The potential energy surfaces (PESs) of the $(\text{HCl})_n(\text{H}_2\text{O})_m$ complexes were calculated by the Hartree–Fock (HF) and Möller–Plesset (MP2) methods using the GAUSSIAN-98 program¹⁹ adapted for use on Pentium PCs. In our approach we applied the Pople's split-valence double-zeta plus polarization basis set 6-31G (d, p). This basis set includes external polarized d- and p-functions at the Cl, O, and H atoms. Besides, the 6-31++G(3df, 3pd) basis set with diffuse functions and the correlation-consistent basis set aug-cc-pVDZ were used.

Tables 1 and 2 present the results of *ab initio* calculations of the geometric and energy characteristics of the HCl and H_2O monomer molecules and their complex $\text{H}_2\text{O}\dots\text{HCl}$ in the configuration of absolute PES minimum. Harmonic vibration frequencies of the monomers and of the complex are given in Tables 3 and 4.

For a comparison, the tables include both the experimental data and the data calculated with the allowance for the electron correlation by the Möller–Plesset perturbation theory.

The data presented in Table 1 evidence of a rather low sensitivity of the geometric parameters to extension of the basis set. The discrepancy with the experimental results for the length of the O–H bond is ~ 0.015 Å when using the HF method. The allowance for the electron correlation leads to better agreement with the experiment.

Table 1. Molecular properties of the H₂O and HCl molecules

Parameter	6-31G(d,p) HF	6-31++G (3df,3pd) HF	6-31G(d,p) MP2	6-31++G (3df,3pd) MP2	Aug-cc- pVDZ HF	Aug-cc- pVDZ MP2	Exp. Ref. 21
H ₂ O							
$r(\text{O-H})$, Å	0.943	0.942	0.961	0.958	0.944	0.966	0.958
$\alpha(\text{HOH})$, deg	106.0	106.3	103.7	103.8	106.0	103.9	104.5
μ , D	2.148	1.948	2.201	2.0	1.96	2.02	1.847
E , a.u.	-76.02361	-76.040899	-76.219785	-76.297593	-76.041843	-76.260910	-
HCl							
$r(\text{Cl-H})$, Å	1.266	1.265	1.269	1.271	1.278	1.288	1.274
μ , D	1.471	1.178	1.475	1.184	1.244	1.256	1.093
E , a.u.	-460.066214	-460.074749	-460.205446	-460.269626	-460.09262	-460.251823	-

Table 2. Structure and energy parameters of the H₂O...HCl complex

Basis set	O-H, Å	O...H, Å	H-Cl, Å	HOH, deg	O...HCl, deg	HO...H, deg	Cl...O, Å	-E, a.u.	-ΔE, a.u.
HF/6-31G(d,p)	0.944	1.975	1.278	106.8	178.5	120.7	3.25	536.098081	5.2
MP2/6-31G(d,p)	0.963	1.862	1.288	104.8	177.6	111.6	3.15	536.437692	7.8
HF/6-31++G(3df, 3pd)	0.942	2.096	1.274	106.7	178.1	122.5	3.37	536.121840	3.89
MP2/6- 31++G(3df, 3pd)	0.960	1.855	1.287	104.3	177.8	110.7	3.14	536.576767	5.99
HF/aug- cc-pVDZ	0.944	2.067	1.286	106.5	178.6	124.5	3.35	536.141111	4.17
MP2/aug cc-pVDZ	0.967	1.856	1.307	104.5	178.8	114.3	3.16	536.522601	6.19

Table 3. Frequencies of harmonic vibrations ω_i and IR intensities A calculated for H₂O and HCl monomers

Assignment	HF/6-31G(d,p), ω_i , cm ⁻¹ , (A , km/mol)	HF/6-31++G (3df, 3pd), ω_i , cm ⁻¹ , (A , km/mol)	MP2/6-31G(d,p), ω_i , cm ⁻¹ , (A , km/mol)	MP2/6-31++G (3df, 3pd), ω_i , cm ⁻¹ , (A , km/mol)	Experiment Refs. 24 and 25, ω_i , cm ⁻¹ , (A , km/mol)
$\nu(\text{Cl-H})$	3176 (34)	3148 (54)	3121 (22)	3070 (51)	3042 (39)
$\nu_{\text{as}}(\text{O-H})$	4262 (58)	4269 (89)	4050 (34)	4010 (75)	3942 (40)
$\nu_{\text{s}}(\text{O-H})$	4145 (16)	4147 (20)	3912 (4)	3893 (8)	3832 (2)
$\delta(\text{HOH})$	1770 (104)	1728 (114)	1679 (78)	1655 (73)	1648 (67)

Notes: ν_{s} is symmetric stretching vibration; ν_{as} is antisymmetric stretching vibration; δ is bending vibration.

Table 4. Frequencies of harmonic vibrations ω_i and frequency shifts $\Delta\omega_i$ (cm⁻¹) for H₂O...HCl complex

Basis	$\Delta\omega$ (OH)	$\Delta\omega$ (OH)	$\Delta\omega$ (ClH)	$\Delta\omega$ (HOH)	ν (O...H)	δ_i (OH _b Cl)	δ_0 (OH _b Cl)	δ_i (HOH _b)	δ_0 (HOH _b)
HF/6-31G(d,p)	-6	-5	-161	-5	151	558	446	210	181
HF/6-31++G(3df,3pd)	-51	-17	-115	21	126	461	366	147	94
+VP ^s (2d) ^s (Ref. 14)	-3	-4	-105	1	118	459	351	143	94
Experiment	-	-	-216	-	100	460	-	157	64
			Ref. 11		Ref. 11	Ref. 11		Ref. 22	Ref. 22

Notes: ν are stretching vibrations; δ_i are bending vibration in a plane; δ_0 are out-of-plane bending vibrations of the H₂O molecule.

For the HOH valence angle, $\Delta\alpha$ is $\sim 1.5^\circ$ (HF), and allowance for the correlation effects decreases it down to $\sim 0.6^\circ$. The length of the H-Cl bond is insensitive to extension of the split-valence basis set; the discrepancy Δr (H-Cl) from the experimental value is 0.008 Å, and with the aug-cc-pVDZ basis set it is only 0.003 Å as small. The allowance for the electron correlation with the use of MP2/6-31++G(3df, 3pd) gives $\Delta r = 0.003$ Å, while MP2/aug-cc-pVDZ gives the overestimated value $\Delta r = 0.014$ Å.

Table 2 presents the geometric parameters of the H₂O...HCl complex as obtained by use of different basis sets (HF, MP2). When using the HF and MP2 methods, the maximum discrepancy for intramolecular parameters is ~ 0.02 Å for Δr and $\Delta\alpha \sim 2^\circ$ for the valence angle. For the intermolecular parameters $\Delta R \sim 0.2$ Å and $\Delta\theta \sim 10^\circ$.

Recent experimental data obtained by Kisiel et al.¹⁵ allow a comparison to be made with the cyclic (H₂O)₂HCl complex. It can be seen from Table 5,

which presents the intermolecular geometric parameters, that although the calculations with the use of HF/6-31G(d,p) give correct cyclic structure,²⁰ but the intermolecular lengths of bonds are overestimated as compared with the experimental values. When using MP2/aug-cc-pVDZ, ΔR is 0.02–0.07 Å.

Table 5. Intermolecular geometric parameters of (H₂O)₂HCl complex

Parameter	HF/6-31G(d,p)	MP2/aug-cc-pVDZ	Exp. Ref. 15
Cl ₁ O ₃	3.346	3.022	3.084
O ₃ O ₆	3.099	2.79	2.815
Cl ₁ O ₆	3.677	3.383	3.415
O ₃ H ₂	2.111	1.778	1.831
O ₆ H ₄	2.228	1.875	1.943
Cl ₁ H ₇	2.946	2.610	2.810
O ₃ H ₄ O ₆	150.9	154.1	149.1
Cl ₁ H ₂ O ₃	160.9	165.9	164.0
Cl ₁ H ₇ O ₆	135.3	137.4	122.0

As can be seen from the above results, to study weakly bound complexes, it is important to include dispersion forces into consideration through making allowance for the electron correlation at optimization of the geometry. The geometric parameters of the complexes (H₂O)₂(HCl)₂ and (H₂O)₃(HCl)₃ were optimized with the use of MP2/aug-cc-pVDZ and MP2/6-31G(d,p) basis sets, respectively.

The aim of this work was to obtain the geometric characteristics and $\Delta\nu$ corresponding to the shifts of the vibration frequencies ν at the formation of complexes.

Table 3 gives the corresponding harmonic frequencies ω_i of the H₂O and HCl monomers for different basis sets and calculation methods. Addition of the diffusion functions does not lead to a considerable change in the harmonic frequencies ω_i . The discrepancy between the calculated, $\omega_{i\text{calc}}$, (HF) and experimental frequencies, $\omega_{i\text{exp}}$, is 4–9%. The allowance for the electron correlation effects (MP2/6-31++G(3df, 3dp), MP2/6-31G(d,p)) decreased $\Delta\omega_i$ down to 1–2%. When comparing the calculated frequencies ω_i and the observed fundamental frequencies ν_i that effectively include the anharmonicity of vibrations, one should keep in mind the difference between $\nu_{i\text{exp}}$ and $\omega_{i\text{exp}}$. For the considered H₂O and HCl monomers, $\omega_{i\text{exp}}$ differs from $\nu_{i\text{exp}}$ by 3–5%.

Table 4 gives the shifts $\Delta\omega_i$ for the heterodimer H₂O...HCl with respect to the monomers' frequencies along with the intermolecular harmonic frequencies obtained for different basis sets. For the relative values of the frequency shifts, the allowance for the electron correlation is not so important as for their absolute values.

The use of calibration functions with the coefficients determined by least-squares method can be one of the methods for effective consideration of vibration anharmonicity in complexes. We propose the use of a linear calibration function

$$\nu_{\text{corr}} = a + b \cdot \omega_{\text{calc}},$$

where a and b are the calibration parameters; ω_{calc} are the calculated (HF/6-31G(d,p)) harmonic frequencies;

ν_{corr} are the corrected values of the vibration frequencies. The experimental values of the monomers' frequencies ν (exp.) presented in Table 6 are used to determine the parameters of the function.

Table 6. Calculated ω_i and corrected ν_{corr} frequencies in the H₂O and HCl monomers

HF/6-31G(d,p), ω_i , cm ⁻¹	ν_{exp} , cm ⁻¹	ν_{corr} , cm ⁻¹
3176	2886	2850
4262	3756	3795
4145	3657	3693
1770	1595	1627

The parameters a and b determined with the use of the calibration function by least-squares method are equal to 87 cm⁻¹ and 0.87, respectively, and the mean absolute discrepancy between ν_{corr} and ν_{exp} is 34 cm⁻¹. The coefficient of correlation between the experimental and calculated frequencies is 0.998.

Results and discussion

Energy stability of (H₂O)_n(HCl)_n complexes and their structure peculiarities

The complex (H₂O)_n(HCl)_n with the even number of molecules $n = 2$ is characterized by the cyclic structure (Fig. 1, Table 7) with $\Delta E = -22.4$ kcal·mol⁻¹ and the total energy $E = -1073.061328$ a.u. (MP2/aug-cc-pVDZ). The complex (H₂O)_n(HCl)_n with $n = 3$ forms a closed plane structure (Fig. 2, Table 8) with the energy of monomer interaction of -37.35 kcal·mol⁻¹ and the total energy $E = -1609.335210$ a.u. (MP2/6-31G(d,p)).

For the complex (H₂O)₂(HCl)₂, the H–Cl bond becomes considerably longer (Δr is ~ 0.02 – 0.06 Å) as compared with the monomer HCl, while the O–H bond elongates less significantly (~ 0.001 – 0.003 Å). As compared with the (H₂O)₂HCl complex, addition of one more HCl molecule leads to shortening of the intermolecular bonds: $\Delta R(\text{O}–\text{O})$ is 0.05 Å and $\Delta R(\text{Cl}–\text{O})$ is 0.04–0.08 Å. As compared with the heterodimer H₂O...HCl, where $\Delta R(\text{Cl}–\text{O})$ is 0.215 Å, and $\Delta R(\text{O}–\text{O}) = 0.18$ Å as compared with the water dimer (H₂O)₂.

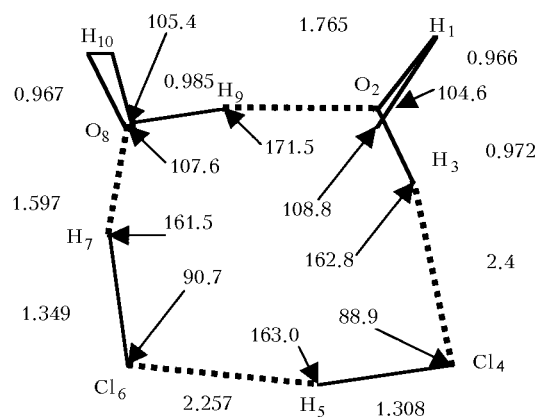
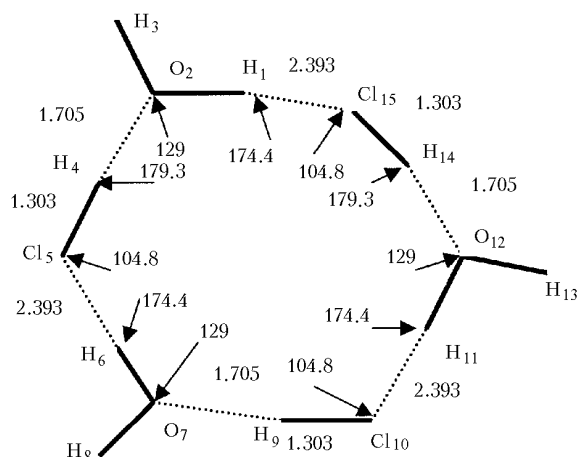


Fig. 1. Geometry of (H₂O...HCl)₂ complex.

Table 7. Cartesian coordinates (Å) for (H₂O)₂...(HCl)₂ complex (MP2/aug-cc-pVDZ)

#	Atomic number	X	Y	Z
1	1	1.273	2.690	0.888
2	8	0.937	2.277	0.082
3	1	1.431	1.443	0.009
4	17	1.970	-0.886	-0.204
5	1	0.702	-1.168	-0.053
6	17	-1.536	-1.336	0.188
7	1	-1.666	0.002	0.067
8	8	-1.718	1.594	-0.049
9	1	-0.790	1.925	-0.019
10	1	-2.077	1.912	-0.889

**Fig. 2.** Geometry of (H₂O...HCl)₃ complex.**Table 8. Cartesian coordinates (Å) for (H₂O)₃...(HCl)₃ complex (MP2/6-31G(d,p))**

#	Atomic number	X	Y	Z
1	1	2.540	0.0	0.614
2	8	2.495	0.0	1.579
3	1	3.405	0.0	1.888
4	1	1.120	0.0	2.589
5	17	0.078	0.0	3.372
6	1	-1.802	0.0	1.891
7	8	-2.616	0.0	1.370
8	1	-3.338	0.0	2.005
9	1	-2.803	0.0	-0.325
10	17	-2.960	0.0	-1.619
11	1	-0.737	0.0	-2.504
12	8	0.121	0.0	-2.948
13	1	-0.066	0.0	-3.890
14	1	1.683	0.0	-2.263
15	17	2.882	0.0	-1.754

The complex (H₂O)₃(HCl)₃ is characterized by a decrease of the intermolecular Cl–O bond with $\Delta R(\text{Cl–O}) = 0.142 \text{ \AA}$ as compared with the heterodimer H₂O...HCl and elongation of the Cl–O bond as compared with the complex (H₂O)₂(HCl)₂ by $\Delta R(\text{Cl–O}) = 0.06 \text{ \AA}$. For the H–Cl intramolecular bond, the elongation with respect to the monomer HCl is 0.015 \AA , and the elongation of the (O–H)_b bond taking part in the hydrogen bonding is 0.003 \AA .

Vibrational spectra of (H₂O)_n(HCl)_n complexes

As was noted in the previous section, the calculated harmonic frequencies ω_i can differ significantly from the experimentally observed frequencies ν_i of the fundamental vibrational transitions. This discrepancy is caused, on the one hand, by the errors of HF method in calculating the ω_i and, on the other hand, with the contributions of anharmonic terms to ν_i when describing vibrational spectra of complexes with the hydrogen bonds. The shift $\Delta\omega = \omega_{\text{monomer}} - \omega_{\text{complex}}$ of the harmonic frequency of vibrations in the HCl molecule as calculated by the HF/6-31G(d,p) method is 161 cm^{-1} for the complex H₂O...HCl (see Table 4), while the experimental¹¹ $\Delta\nu = \nu_{\text{monomer}} - \nu_{\text{complex}} = 216 \text{ cm}^{-1}$. However, we should take into account that the use of N₂ matrix leads to a larger shift as compared with the gas phase (for similar systems in Ref. 11, the shift $\Delta\nu$ in the gas phase is 1.8 times smaller than $\Delta\nu$ with the use of the N₂ matrix). The anharmonic red shift obtained in Ref. 23 is 157 cm^{-1} . Thus, the frequency shift value determined as described above can be thought correct enough. The calculated ω_i and corrected ν_i frequencies of the complexes (H₂O)_n(HCl)_n are given in Tables 9–11. The calculation predicts red shift of the frequency ν_{HCl} and the increase in the intensity of the corresponding spectral line.

Table 9. Frequencies of intermolecular vibrations in (H₂O)₂...(HCl)₂ complex (HF/6-31G(d,p))

$\omega_i, \text{ cm}^{-1},$ (A, km/mol)	$\nu_{i,\text{corr}}, \text{ cm}^{-1}$	$\Delta\nu_i, \text{ cm}^{-1}$
1776 (114)	1632	+5
1794 (73)	1648	+21
2825* (212)	2545	-305
3119* (254)	2801	-49
4014 (89)	3579	-114
4129 (62)	3679	-14
4226 (124)	3764	-31
4241 (139)	3777	-18

* ν is the stretching vibration of the H–Cl bond.

Table 10. Frequencies of intermolecular vibrations in (H₂O)₃...(HCl)₃ (HF/6-31G(d,p))

$\omega_i, \text{ cm}^{-1},$ (A, km/mol)	$\nu_{i,\text{corr}}, \text{ cm}^{-1}$	$\Delta\nu_i, \text{ cm}^{-1}$
1777 (107)	1633	+6
1777 (106)	1633	+6
1782 (0)	1637	+10
2859* (0)	2574	-276
2874* (1228)	2587	-263
2874* (1226)	2587	-15
4127 (0)	3678	-13
4130 (201)	3680	-13
4249 (0)	3680	-11
4249 (259)	3784	-11
4249 (260)	3784	-11

* ν is the stretching vibration of the H–Cl bond.

Table 11. Frequencies of intermolecular vibrations in (H₂O)_n...(HCl)_n complexes (HF/6-31G(d,p))

$\omega_i, \text{cm}^{-1}, (A, \text{km/mol})$ (H ₂ O) ₂ ...(HCl) ₂	$\omega_i, \text{cm}^{-1}, (A, \text{km/mol})$ (H ₂ O) ₃ ...(HCl) ₃
23 (1)	8 (1)
44 (1)	13 (10)
83 (5)	13 (0)
85 (4)	31 (2)
140 (52)	31 (2)
174 (10)	57 (0)
212 (71)	73 (0)
221 (77)	87 (12)
244 (86)	87 (12)
268 (70)	109 (0)
290 (122)	109 (0)
389 (60)	192 (10)
431 (163)	192 (10)
558 (59)	197 (0)
680 (234)	278 (0)
799 (143)	279 (0)
	289 (0)
	312 (65)
	312 (65)
	315 (580)
	504 (0)
	504 (0)
	513 (295)
	669 (145)
	669 (145)
	702 (0)

Conclusion

The performed *ab initio* calculations of the complexes of water and hydrogen chlorine (H₂O)_n...(HCl)_n {2:2; 3:3} refine the characteristics and improve the assignment of the IR spectra of water vapor mixed with hydrogen chloride under atmospheric conditions.

In all (H₂O)_n...(HCl)_n {2:2; 3:3} complexes, the value of ν (HCl) shifts to lower frequencies. This shift for the considered complexes falls within the following frequency range $\Delta\omega$ (cm⁻¹): from -40 to -300. The other group of the low-frequency vibrations corresponds to the intermolecular vibrations of the (H₂O)_n...(HCl)_n complexes and falls in the frequency range ~ 10–800 cm⁻¹.

The geometry of the considered complexes is characterized by manifestation of the cooperative nature of the intermolecular interactions, which results in a decrease of the length of the hydrogen bond between heavy atoms with respect to the heterodimer H₂O...HCl and dimer H₂O...H₂O.

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