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Ab initio study of spectroscopic constants and anharmonic force field of hypochlorous acid $HO^{35}Cl$

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Abstract. The molecular geometries, spectroscopy constants, and anharmonic force field of hypochlorous acid have been calculated at B3PW91, MP2, CCSD(T) levels of theory employing three basis sets, 6-311g(3df,2p), 6-311g(3df,3pd) and cc-pVQZ, respectively. The equilibrium structures, rotational constants, anharmonicity constants, vibration-rotation interaction constants, quartic and sextic centrifugal distortion constants are compared with the available experimental data. Coriolis coupling constants are also calculated here. The partial spectroscopy constants show that the MP2 represent an improvement over the results obtained from B3PW91. The CCSD(T) method is also a good choice to study the anharmonic force field of this molecule.

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Key words: Anharmonic force field; spectroscopy constant; Ab initio study; hypochlorous acid.

1 Introduction

The molecules containing chlorine atoms are believed to act an important role in the atmosphere pollution and have attracted extensive attention. Hypochlorous acid (HOCl) which contains chlorine atom is considered to be a temporary reservoir for active chlorine and dissociates photochemically to produce chlorine atoms. Until now, it is believed to play a more important role in ozone depletion on polar stratospheric clouds [1, 2].

$$
\begin{aligned}
&HOCl+hv\rightarrow HO+Cl\\
&OH+O_3\rightarrow HO_2+O_2\\
&Cl+O_3\rightarrow ClO+O_2\\
&HO_2+ClO\rightarrow HOCl+O_2
\end{aligned}
$$

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In order to prevent the ozone hole from the further expansion, it is essential to get a better understanding of the properties of atmospheric molecule that participate in ozone depletion and of the chemical reactions themselves. Thus, a number of experimental and theoretical investigations have been undertaken in order to learn more about the properties of Hypochlorous acid (HOCl). As early as 1951, Hedberg and Badger [3] studied the initial infrared spectroscopy of HOCl and its isotopomer DOCl. Data of equilibrium rotational constants for HOCl and DOCl were determined from a lower resolution work by Deeley [4]. The near infrared high-resolution spectra [5] of the weak $3v_1$+$2v_2$ combination band of HOCl35(37) at 12600cm^{-1} were recorded in an ultrasensitive titanium: sapphire intracavity laser absorption spectrometer (ICLAS). The high resolution far-infrared spectrum [6] of HOCl were recorded between 20 and 360cm^{-1} by means of Fourier transform spectroscopy, which can observe the pure rotation lines involving rotational levels. Bellini *et al.* [7] reported the pure rotational spectrum of HOCl35(37) in the sub-millimeter wave region, from which one could obtain the rotational constants, quartic and sextic centrifugal distortion constants.

There have been a number of theoretical calculations on HOCl. Halonen and Ha [8] performed an *ab initio* calculation at MP3 level to determine the equilibrium structure and the anharmonic force field of this molecule. Escribano *et al.* [9] evaluated the geometrical parameters and determined the anharmonic force constants involving the equilibrium moments of inertia. From *ab initio* and scaled *ab initio* potential surfaces, Zhang and Ramachandran [10] reported the spectroscopic constants and anharmonic force fields for the HOCl and DOCl. From 1998 to 2000, Peterson *et al.* [11, 12-16] finished many theory computations about this molecule and its isotopomers on accurate *ab initio* potential energy surfaces.

The molecule is known to exhibit strong electron correlation effects, and it is therefore of interest to compare the quality of their B3PW91, MP2, and CCSD(T) anharmonic force fields. B3PW91 is the simplest correlated scheme but it has been rarely applied to this molecule. MP2 and CCSD(T) have all been applied and successfully in this area with very large basis sets.

In comparison to the present calculations, the former work has calculated the geometry, rotational constants, vibration-rotation constants, fourth centrifugal distortion constants, and quadratic, cubic, and quartic force constants in dimensionless normal coordinates, but they rarely calculated and discussed the quartic force constants and the sixth centrifugal distortion constants. In order to accurately calculate rotational spectra of molecules, it is necessary to take them into account. In the present case, we calculate the equilibrium geometry structure and the anharmonic force field by B3PW91, MP2, and CCSD(T) with 6-311g(3df,2p), 6-311g(3df,3pd) and cc-pVQZ basis sets.

2 Details of the calculations

All quantum-chemical calculations were carried out at B3PW91, MP2, and CCSD(T) levels using GAUSSIAN03 [17] and ACESII [18]. Three different basis sets were employed:

6-311g(3df,2p) (A for short in this text), 6-311g(3df,3pd)(B for short), cc-pVQZ(C for short). The third basis is the correlation-consistent polarized valence quadruple-zeta (cc-pVQZ), where H is the [4s,3p,2d,1f] contraction of a (6s,3p,2d,1f) primitive set [19], O is the [5s,4p,3d,2f,1g] contraction of a (12s,6p,3d,2f,1g) primitive set [19], and Cl is the [6s,5p,3d,2f,1g] contraction of a (16s,11p,3d,2f,1g) primitive set [19]. The other basis sets have the similar explanation.

Spectroscopic parameters include the harmonized wave numbers and quartic centrifugal distortion constants of ground vibrational states in the case of harmonic force field calculations, and the vibration-rotation interaction constants and the vibrational anharmonicity constants in the case of anharmonic force field calculations. For the asymmetric top molecules, the vibrational dependence of rotational constants is customarily expanded in the Taylor series [20]

$$A_v = A_e - \sum_i \alpha_i^A \left(v_i + \frac{1}{2} \right) + \cdots, \tag{1}$$

Where v_i is the vibrational quantum number for the ith vibrational normal mode. Similar expressions hold for the rotational constants B_v and C_v . The anharmonicity constants χ are defined in the formula of the vibrational term for an asymmetric top:

$$G(v)/hc = \sum_r \omega_r (v_r + \frac{1}{2}) + \sum_{r \prec s} \chi_{rs} (v_r + \frac{1}{2})(v_s + \frac{1}{2}) + \cdots, \tag{2}$$

where the summations are over the normal modes.

Using the analytic energy gradients, the molecular geometries were optimized under the constraint of C_s symmetry for HOCl. At the computed equilibrium geometries, harmonic force fields were evaluated analytically. Harmonic force constants without inner-shell correlation contributions were evaluated numerically from energies. The normal modes and the harmonic spectroscopic constants were obtained in the usual manner [21, 22]. Cubic and semi-diagonal quartic normal coordinate force constants were calculated at MP2, B3PW91, and CCSD(T) levels for the three basis sets. They were determined with the use of a finite difference procedure [18] involving displacements along the reduced normal coordinates and the calculation of analytic second derivatives at these displaced geometries. The anharmonic spectroscopic constants were derived from the theoretical normal coordinate force fields applying the standard formulas based on second-order rovibrational perturbation theory [23, 24].

3 Results and discussion

The results of our calculations are collected in Tables 1-4. The molecular geometries, the spectroscopic constants, and the full quartic force fields of HOCl are compared with the available experimental or empirical data.

Table 1: Molecular equilibrium geometries and electric dipole moment of HOCl^a.

	B3PW91			MP2			CCSD(T)	Pre.		Exp.
parameter	A	B	VQZ	A	B	C	C	Ref.8	Ref.11	(Ref.4)
r	0.9643	0.9643	0.9642	0.9654	0.9643	0.9654	0.9622	0.973	0.9643	0.9643(5)
R	1.6875	1.6865	1.6890	1.6890	1.6888	1.6885	1.6947	1.705	1.6939	1.6891(2)
A	102.92	103.24	103.19	102.44	102.54	102.45	102.66	103.2	102.82	102.96(8)
μ	1.608	1.557	1.557	1.595	1.520	1.541	1.531		1.510	1.515(2)^b

[a] bond lengths in Å, bond angles in deg, and dipole moments in Debye.

[b] Ref[25].

Table 2: Rotational constants of equilibrium and ground states of HOCl (cm^{-1}).

	B3PW91			MP2			CCSD(T)	Pre.^{b}	Exp.
constant	A	B	C	A	B	C	C	Ref.11	
A_e	20.48988	20.55695	20.54873	20.35548	20.420575	20.35856	20.52942	20.4707	20.49760^a
B_e	0.50824	0.50865	0.50715	0.50768	0.50773	0.50795	0.50422	0.5046	0.50735^a
C_e	0.49594	0.49637	0.49494	0.49533	0.49541	0.49559	0.49213	0.4924	0.49509^a
A_0	20.40876	20.48214	20.47821	20.24578	20.31632	20.25285	20.47080	20.4144	20.46362^c
B_0	0.50584	0.50627	0.50478	0.50488	0.50495	0.50521	0.50117	0.5016	0.50429^c
C_0	0.49273	0.49318	0.49175	0.49171	0.49182	0.49203	0.48835	0.4887	0.49123^c

[a] Ref[9].

[b] The previous computed results (Ref.10) are not shown here.

[c] Ref[26].

The calculated and experimentally derived [4] equilibrium molecular parameters of hypochlorous acid are given in Table 1. There is an excellent agreement between theory and experiment for the OH bond length by B3PW91, where all theoretical values lie within the experimental uncertainty. The OH bond length by MP2 with 6-311g(3df,3pd) reproduces the experimental value, whereas the result for CCSD(T) with cc-pVQZ underestimated by 0.0021 Å. The OCl bond length is underestimated by B3PW91 (up to 0.0001-0.0026 Å) and overestimated by CCSD(T) (up to 0.0056 Å). The computed bond angle ∠HOCl angle deviates the experimental value within 0.04° by B3PW91 with 6-311g(3df,2p). The HOCl angle calculated by MP2 and B3PW91 are all smaller than the experimental values.

Table 1 also compares theoretical and experimental [4] dipole moments of HOCl. All the computed values (1.608-1.520D) seem to be higher than the experimental value (1.515D). The previous computed results are also listed in Table 1 [8, 11, 25].

Table 2 lists the computed rotational constants for HOCl at B3PW91, MP2, and CCSD(T) along with the available experimental data [9, 26]. The theoretical ground-state rotational constants (A_0,B_0,C_0) have been obtained from the associated equilibrium constants (A_e,B_e,C_e) by taking into account the effects of vibration-rotation coupling via perturbation theory [23, 24]. We can see that the calculated rotational constants reproduce well with the experimental values except for the A_e, which the derivation is about 0.05935-0.14212cm^{-1}. The previous computed results are also listed in Table 2 [10, 11].

Table 3: Harmonic and fundamental vibrational wave numbers of HOCL(cm^{-1}).

	B3PW91			MP2			CCSD(T)	Pre.^{b}	Exp.	
constant	A	B	C	A	B	C	C	Ref.11		
ω_1	3814.7	3813.5	3803.7	3808.4	3840.0	3796.7	3814.4	3801.8	3815.45^{a}	3794.1^{d}
ω_2	1278.4	1274.8	1269.5	1279.5	1265.7	1271.2	1279.1	1273.3	1269.18^{a}	1272.1^{d}
ω_3	763.4	764.5	765.7	765.3	765.0	771.5	743.1	740.2	741.9^{a}	739.3^{e}
v_1	3628.24	3632.39	3626.28	3621.40	3647.88	3613.2	3629.8	3614.0	3609.48^{b}	
v_2	1249.29	1245.69	1242.05	1247.78	1235.87	1237.8	1245.3	1238.1	1238.62^{c}	
v_3	750.80	752.02	753.44	751.67	751.42	758.3	727.8	724.7	724.36^{c}	

[a] Ref[8].

[b] Ref[27].

[c] Ref[28].

[d] Ref[29].

[e] Ref[5].

Table 4: Anharmonic constants χ_{ij} of HOCl(cm^{-1}).

	B3PW91			MP2			CCSD(T)	Pre.		Exp.
constant	A	B	C	A	B	C	C	Ref.8	Ref.11	(Ref.29)
X_{11}	-87.72	-85.28	-83.39	-86.53	-89.27	-84.5	-85.22	-97.50	-87.0	-85.55
X_{12}	-20.89	-19.98	-20.27	-24.87	-24.27	-25.88	-26.33	-21.22	-28.6	-26.16
X_{13}	-1.23	-1.08	-1.05	-3.02	-2.87	-2.88	-2.07	-0.72	-2.8	-1.93
X_{22}	-7.50	-7.73	-6.85	-7.55	-6.81	-8.14	-8.08	-8.01	-8.2	-7.64
X_{23}	-7.42	-7.31	-7.21	-8.35	-8.23	-8.28	-8.88	-7.85	-8.8	
X_{33}	-4.15	-4.15	-4.07	-3.98	-4.01	-3.81	-4.92	-6.63		

Table 3 presents the calculated harmonic and fundamental vibrational wave numbers for HOCl. The vibrational quantum numbers v_1 and v_3 stand for the HO and OCl bond stretching modes, and v_2 stands for the HOCl bending mode. The theoretical fundamental wave numbers were derived from the corresponding harmonic wave numbers and anharmonicity constants. All harmonic and fundamental values of HOCl are known accurately from experiment [5, 8, 27, 28, 29]. As we see, the harmonic experimental wave numbers have two groups values [5, 24, 28]. Here our calculated values for ω_1 and ω_2 just lie between the two groups experimental values, whereas ω_3 is too high by 4-32cm^{-1}. The calculated values by MP2/cc-pVQZ show good agreement with experiment except for ω_3(771.5cm^{-1}) and v_3(758.3cm^{-1}). The calculations overestimate the fundamental wave numbers: For example, the MP2/6-311g(3df,3pd) value are too high by 38.4cm^{-1} for HO bond stretching mode, the MP2/cc-pVQZ value are high by 33.94cm^{-1} for OCl bond stretching mode.

Table 4 shows the calculated anharmonicity constants χ_{ij} with experimental values [29] (except for X_{23} and X_{33}). Basis set effects on the calculated anharmonicity constants are generally quite small, both at the B3PW91 and MP2. The CCSD(T) results deviate from the available experimental data by less than 0.5cm^{-1}, so it can provide the reliable prediction of the unknown experimental values. The MP2 results are often also satisfac-

Table 5: Vibration-rotation interaction constants of HOCl(cm^{-1}).

	B3PW91			MP2			CCSD(T)	Pre.	Exp.
constant	A	B	C	A	B	C	C	Ref.11	(Ref.8)
α_1^A	0.7731	0.7667	0.7574	0.7998	0.7944	0.7873	0.7843	0.78	0.7960
α_2^A	-0.6313	-0.6379	-0.6374	-0.6056	-0.6107	-0.6000	-0.6980	-0.7007	-0.7631
α_3^A	0.02044	0.02087	0.02086	0.02522	0.02474	0.02408	0.03087	0.03068	0.03110
$\alpha_1^B/10^{-3}$	0.41	0.39	0.39	0.90	0.89	0.89	0.6971	0.6905	0.6194
$\alpha_2^B/10^{-3}$	0.43	0.41	0.46	0.62	0.57	0.64	0.9185	0.8439	0.8068
$\alpha_3^B/10^{-3}$	3.95	3.96	3.90	4.08	4.10	3.97	4.480	4.450	4.587
$\alpha_1^C/10^{-3}$	0.79	0.76	0.76	1.28	1.26	1.26	1.053	1.047	0.9813
$\alpha_2^C/10^{-3}$	1.75	1.74	1.79	1.95	1.90	1.97	2.085	2.018	2.131
$\alpha_3^C/10^{-3}$	3.87	3.88	3.82	4.0	4.01	3.88	4.436	4.409	4.545

tory, but there are two values with larger deviations (3.72cm^{-1} for X_{11} and 1.89cm^{-1} for X_{12} by 6-311g(3df,3pd) basis). B3PW91 generally yields somewhat lower values than the experiment: for example, the 6-311g(3df,3pd) value are too low by 6.08cm^{-1} for X_{12}. The previous computed results are also listed in Table 4 [11, 28]. Finally, the effects of a possible Fermi resonance between the HOCl bending fundamental v_2, and the first overtone of the OCl stretching mode $2v_3$ of the HOCl molecule have been investigated.

The calculated vibration-rotation interaction constants $\alpha_i^X (X = A,\ B,\ C;\ i = 1-3)$ are collected in Table 5 together with the corresponding experimental data [11] for HOCl. Comparing the theoretical results with each other, it is obvious that there are often appreciable changes (e.g., α_1^B, α_2^B, α_1^C, α_2^C) when going from the MP2 to the CCSD(T) level, whereas the basis set dependence at a given level [MP2 or CCSD(T)] is normally less pronounced. In particular, relative to B3PW91/6-311g(3df,2p), the enhancement of the basis to B3PW91/6-311g(3df,3pd) generally causes much smaller changes in the calculated vibration-rotation constants than the transition to MP2/6-311g(3df,2p) (higher theoretical level, same basis). The CCSD(T) results usually turn out to be more reliable. In the absence of Coriolis resonances the calculated CCSD(T) values are normally close to the experimental ones.

From Table 5 we can see that our calculated results are generally with correct sign and with reasonable magnitude. In a more quantitative evaluation, the CCSD(T) results are significantly better than the B3PW91 and MP2 results. The relative errors of the CCSD(T) values are normally below 12.54%, whereas those of the B3PW9 values may range up to 49% and the MP2 values may range up to 45%. Here there is a negative value of α_2^A, which as previously shown by Palmiei *et al* [30]. for HOBr, is sensitive to small changes in the cubic force constants.

The equilibrium quartic centrifugal distortion constants (S-reduction) shown in Table 6 with the experimental ground-state datas [31]. The best overall agreement is found at CCSD(T)/cc-pVQZ. The B3PW91 and MP2 calculations underestimate the experimental values. At the same time, we can see that basis set effects is generally quite small with

Table 6: Equilibrium quartic centrifugal distortion constants of HOCl (Hz) (S-reduction).

	B3PW91			MP2			CCSD(T)	Pre.	Exp.
constant	A	B	C	A	B	C	C	Ref.11	(Ref.31)
$D_J \times 10^6$	0.0252	0.0252	0.0249	0.0250	0.0250	0.0246	0.0260	0.0262	0.026911
$D_{JK} \times 10^6$	1.1736	1.1889	1.1815	1.1957	1.2150	1.1976	1.1819	1.190	1.25312
$D_K \times 10^6$	92.10	94.33	94.46	90.28	90.40	90.81	111.75	112.4	129.959
$d_1 \times 10^3$	-0.551	-0.548	-0.542	-0.543	-0.542	-0.536	-0.560	-0.57	-0.6259
$d_2 \times 10^3$	-0.033	-0.033	-0.033	-0.033	-0.034	-0.033	-0.032	-0.03	-0.0448

Table 7: Sextic centrifugal distortion constants of HOCl (Hz) (S-reduction).

	B3PW91			MP2			Pre.	Exp.
constant	A	B	C	A	B	C	Ref.12	(Ref.7)
H_J	-0.005246	-0.005408	-0.0046	-0.0080535	-0.0085315	-0.006033	-0.014	-0.012537
H_{JK}	297.5054	308.8383	301.7514	264.2705	261.08167	255.3855	2.94	3.35635
H_{KJ}	45989.584	49430.626	49462.128	42773.02	44354.813	43351.426	619	971.290
H_K	0.41282	0.429969	0.32468	0.095361	0.12458	0.052567	88200	119284.07
h_1(mhz)	1.7277	1.722798	1.7239	1.5891	1.59857	1.6394	0.22	-0.4920
h_2(mhz)	0.2206	0.2206	0.215146	0.20886	0.21362	0.2062	0.33	0.82048
h_3(mhz)	0.03178	0.03206	0.03190	0.031649	0.032692	0.032278	0.03	0.060457

the same method. It needs to notice that comparing computed equilibrium centrifugal distortion constants with available experimental ground-state values may be problematic if the differences between the experimental equilibrium and computed ground-state values are not negligible.

The equilibrium sextic centrifugal distortion constants (S-reduction) calculated from B3PW91 and MP2 are shown in Table 7 with the experimental ground-state datas [7]. There is a big discrepancy about magnitude between the computed values and experimental values except for h_2 and h_3. The experimental value of h_1 is negative sign, but our theory values are positive. All our calculation values are with the same sign and with the same magnitude. The above results show that comparing computed equilibrium centrifugal distortion constants with available experimental ground-state values may be problematic if the differences between the experimental equilibrium and computed ground-state values are not negligible.

Table 8 gives the effective quadratic, cubic and quartic normal coordinate force constants of HOCl molecule calculated from the *ab initio* force field and of the previous work from Halonen *et al.* [8] By definition, the quadratic normal coordinate constants correspond to the harmonic wave numbers. The values with the same method close to each other. The discrepancy can not be neglected between MP2 and B3PW91 even if with the same basis set. Overall, the values of B3PW91 seem to be closer to the previous values [8]. Note that the effective force constants are defined in terms of the normal coordinates of the HOCl molecule. Therefore, the calculated values can have different signs resulting from different phase factors of the normal coordinates .

Table 8: Quadratic, cubic and quartic force constants of HOCl in normal coordinates (cm^{-1}).

	B3PW91			MP2			CCSD(T)	Pre.	
constant	A	B	C	A	B	C	C	Ref.8	
ω_1	3814.7	3813.5	3803.7	3808.4	3840.0	3796.7	3814.4	3815.45	3794.1^d
ω_2	1278.4	1274.8	1269.5	1279.5	1265.7	1271.2	1279.1	1269.18	1272.1^d
ω_3	763.4	764.5	765.7	765.3	765.0	771.5	743.1	741.9	739.3^e
111	2594.7	2581.4	2559.1	2599.1	2614.2	2571.4	-2587.2	-2605.8	
112	-22.7	-25.7	-26.3	15.6	8.3	12.0	-0.1	-2.2	
113	-15.7	-14.7	-14.8	-40.7	-39.3	-40.2	28.8	-25.4	
122	-825.5	-827.4	-826.5	-810.7	-843.7	-806.9	817.7	837.5	
123	196.1	196.6	193.8	202.9	208.1	201.3	198.3	-198.4	
133	-47.2	-47.5	-46.2	-52.4	-53.5	-51.6	49.5	54.3	
222	-148.6	-142.3	-140.9	-138.3	-115.1	-126.7	-139.8	-156.9	
223	-56.8	-56.6	-59.4	-65.9	-65.8	-68.5	70.0	-63.7	
233	-22.4	-22.9	-21.7	-19.0	-19.9	-18.6	-17.3	-21.0	
333	-246.2	-246.6	-245.3	-252.9	-253.4	-250.1	264.5	-267.2	
1111	1539.2	1549.4	1537.0	1576.5	1541.8	1553.5	1563.3	1411.7	
1122	-871.0	-865.5	-861.5	-875.2	-898.1	-868.7	-891.3	-887.4	
1133	-41.0	-40.7	-39.3	-44.7	-45.2	-43.5	-41.5	-40.4	
2222	598.4	594.4	608.3	574.6	617.9	556.2	578.0	613.1	
2233	28.3	28.8	28.9	30.3	32.2	30.4	28.2	33.7	
3333	67.7	68.1	67.6	77.7	78.0	76.4	80.1	56.6	

[d] Ref[29].

[e] Ref[5].

Table 9: Coriolis coupling constants ζ_{ij} of HOCl.

	B3PW91			MP2		
ij	A	B	C	A	B	C
21	-0.97651	-0.97651	-0.97683	-0.97552	-0.97554	-0.97564
31	0.15020	0.15035	0.14843	0.15850	0.15871	0.15793
32	0.15449	0.15437	0.15416	0.15246	0.15213	0.15228

Table 9 reports the coriolis coupling constants ζ_{ij} by B3PW91 and MP2. The calculations generally yield the constants with the correct sign and with reasonable magnitude. Our results agree well with each other, although there is no experimental value of coriolis coupling constants.

4 Conclusion

The complete quartic force fields of HOCl has been computed at the B3PW91, MP2 and CCSD(T) level of theory with small basis sets 6-311g(3df,2p), 6-311g(3df,3pd) and large basis set cc-pVQZ for the harmonic and anharmonic parts, respectively. All the computations give excellent molecular equilibrium geometries of HOCl. The small basis sets also give excellent results with the experimental data. MP2/6-311g(3df,3pd) affords a marked improvement over B3PW91/6-311g(3df,3pd). CCSD(T)/ cc-pVQZ show good agreement with experiment in the calculation of anharmonic constants, vibration-rotation interaction constants and quartic centrifugal distortion constants. Furthermore, we find big discrepancy between the computed equilibrium centrifugal distortion constants and the experimental ground-state values in computation of sextic centrifugal distortion constants.

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