

Quantum Mechanical Calculation of Spectroscopic Constants of ClO and ClO⁺

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The *ab initio* calculations were performed on ClO and ClO⁺ using the configuration interaction and Møller-Plesset methods of several different levels of approximation. Three different basis sets, 66 contracted Gaussian-type orbitals, 6-31G* and 6-311G*, were employed in this calculation. The results of calculation were compared with the experimental values of ClO. The values from the calculation with 66cGTO basis set gave excellent agreement with the experimental values. The spectroscopic constants of ClO⁺ were also predicted.

Introduction

The role of chlorine monoxide molecule is thought to be a catalyst in the chlorine cycle for the destruction of ozone in the earth's stratosphere¹. The importance of its role has resulted in much recent interest in ClO spectroscopically and theoretically. The emission spectra of ClO have been first observed by Pannetier and Gaydon² and the absorption spectrum by Poter³, Durie and Ramsay⁴, and Coxon Ramsay⁵. The molecular constants of ClO were assigned with the rotational analysis of the A²I₁-X²I₁ band system by Coxon and Ramsay. Recently Andrews *et al.*⁶ and Hudgens *et al.*⁷ also performed the analysis of the absorption spectrum of ClO.

The rotational spectra of ClO radical in the millimeter and submillimeter wavelength region have been analyzed by Amano and Hirota⁸, and Kakar *et al.*⁹ and the precise molecular parameters have been obtained. Lately the high-resolution infrared spectra of ClO radical have been observed using a Fourier transform spectrometer and a diode laser to calculate the fundamental transition moment of ClO(X²I₁)^{10,11}.

Because of the great interest about its catalytic role in the destruction of stratospheric ozone, numerous attempts have been made for the quantitative measurements of ClO. The techniques to measure atmospheric concentration of ClO have included balloon borne in situ method by atomic resonance fluorescence measurements^{12,13}, millimeter wave heterodyne measurements of ClO emission lines¹⁴⁻¹⁶ and infrared heterodyne measurements¹⁷⁻¹⁹.

There are a few theoretical calculations for ClO. O'Hare and Wahl²⁰ have calculated dissociation energy, ionization potential and dipole moment of ClO, ClO⁻ and ClO⁺. Including the electron correlation energy, Lievin and Metz²¹ have obtained R_e , ω_e and D_e of ClO. Langhoff *et al.*²² have computed the electric dipole moment of ClO using the CI method.

Although there have been a number of works for ClO, there is only one experimental work²³ for ClO⁺, which has observed the structure and vibrational frequencies of ClO⁺. Theoretical calculations of ClO⁺ are also hardly found²⁰.

These molecular ions and radicals are widely distributed in the interstellar medium and the information about those molecular ions have a great deal of effect to understand the chemistry and dynamics in the interstellar medium. And lately a lot of efforts have been concentrated to search those rare molecular ions^{24,25}. The detection of interstellar molecu-

les has been greatly aided by their spectroscopic constants from experiment or theory. Many of the molecular ions have been studied theoretically to obtain the spectroscopic properties and molecular geometries²⁶⁻²⁸.

In this work the molecular parameters of ClO⁺ have been calculated with Møller-Plesset(MP) perturbation method²⁹ and configuration interaction method(CI), and the spectroscopic information has been provided for the further experimental search. The calculations on ClO radical were also performed to compare the data with known experimental values and to obtain the criteria for the error in calculations.

Calculation and Results

ClO⁺. All calculations were performed with the GAUSSIAN 86 and 88 program. Electronic ground state of ClO is ²I₁ with an electronic configuration... $(6\sigma)^2(7\sigma)^2(2\pi)^4(3\pi)^3$. Therefore the electronic configuration of ClO⁺ is likely to be ... $(6\sigma)^2(7\sigma)^2(2\pi)^4(3\pi)^3$, and the lowest electronic state is ³Σ.

Several different levels of single point calculations were carried out. Basis sets of the 66cGTO (66 contracted Gaussian-type orbitals), 6-31G*³⁰(single-zeta core, double-zeta valence, polarization functions on nonhydrogen atoms) and 6-311G* (single-zeta core, triple-zeta valence, polarization functions on nonhydrogen atoms) were used in the calculations. The basis set of 66cGTO consisted of (10s, 6p, 2d) contracted to [7s, 4p, 2d] on the atom, O, and (13s, 9p, 2d) contracted to [9s, 6p, 2d] on the atom, Cl, where only the innermost functions of each symmetry were contracted. Huzinaga's primitives³³ were used for the (10s, 6p) set and the (12s, 9p) set of Veillard³⁴ was modified for the (1s, 9p) set. The *d* exponents were related to the third most diffuse *p* exponents by successive multiplication by 1.5 and 0.5³⁵. The (13s, 9p) set was obtained from the (12s, 9p) primitives of Veillard by replacing the two most diffuse *s* primitives with three by taking the geometric mean and multiplying by 2.5, 1.0 and 0.4³⁵. All electrons were correlated in the MP and CI calculations.

In Figure 1 and 2 the total energies are shown for MP3, MP4SDQ and CISD. Figure 1 is obtained with the basis set of 6-311G* and Figure 2 is obtained with the basis set of 66 cGTO. Using the basis set of the 66cGTO, the total energies were much lower than those of 6-31G* and 6-311G*

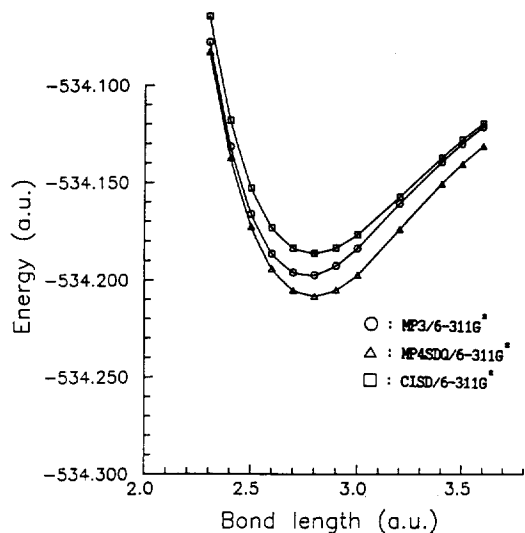


Figure 1. The potential curve of ClO⁺ with 6-311G* basis set.

for all levels of approximation.

The energy points were fit to the polynomials of sixth degree in the internal displacement coordinate $\Delta R = R - R_e$;

$$V - V_0 = \sum_{n=2}^6 f^n \Delta R^n / n !$$

The derived potential constants are listed in Table 1.

In addition, CI calculations were performed with the same basis sets. The CI calculation required about twice longer CPU time than that of MP calculation, but the energies of the CI calculations are higher than those of the MP methods. After the energy points were fit to the potential function,

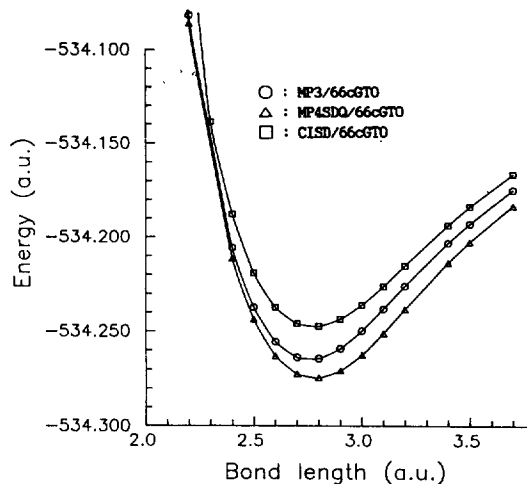


Figure 2. The potential curve of ClO⁺ with 66cGTO basis set.

the potential constants were obtained, and those are shown in Table 2.

From these potential function the various spectroscopic parameters were calculated by the method used in our previous paper³¹. Those values are in Table 3. The bigger basis set gave shorter bond length and smaller ω_e value. The CISD with 66cGTO gave short bond length, which is different from the previous results. The potential functions were different for various method of calculations and the spectroscopic constants were affected by the shape of potential function. For ClO⁺ case no reference was available for the comparison purpose.

Since the molecular structure and spectroscopic properties

Table 1. The Potential Energy Function^a of ClO⁺ with the MP Energies

	basis set	MP3	MP4DQ	MP4SDQ
V_0 (a. u.)	6-31G*	-534.13759	-534.13927	-534.14774
	6-311G*	-534.19723	-534.19855	-534.20823
	66cGTO	-534.26483	-534.26446	-534.27445
R_e (Å)	6-31G*	1.47415	1.47382	1.48752
	6-311G*	1.46437	1.46396	1.47756
	66cGTO	1.46055	1.45722	1.46997
f^2	6-31G*	0.693906	0.658974	0.667586
	6-311G*	0.594924	0.591239	0.616537
	66cGTO	0.602948	0.554240	0.576580
f^3	6-31G*	-2.06669	-2.10124	-1.76051
	6-311G*	-1.99502	-2.02123	-1.74070
	66cGTO	-1.91855	-1.82761	-1.61208
f^4	6-31G*	1.73136	1.81808	2.23093
	6-311G*	2.75814	2.82751	2.49935
	66cGTO	1.80786	2.82685	2.64915
f^5	6-31G*	-18.3075	-17.4416	-25.1212
	6-311G*	-17.2389	-16.7670	-21.7364
	66cGTO	-13.9487	-17.4900	-20.7169
f^6	6-31G*	157.228	154.342	140.911
	6-311G*	108.750	107.086	113.802
	66cGTO	102.161	94.1592	97.8991

^a Atomic units.

Table 2. The Calculated Potential Energy Function^a of ClO⁺ with CI Energies

	CISD/6-31G*	CISD/6-311G*	CISD/66cGTO
V_0 (a.u.)	-534.12750	-534.18627	-534.24742
R_e (Å)	1.48919	1.47771	1.46714
f^2	0.597458	0.548994	0.516785
f^3	-1.88377	-1.83571	-1.69073
f^4	3.81835	3.980622	3.77578
f^5	-21.2796	-19.2645	-18.8842
f^6	102.111	80.2665	72.8912

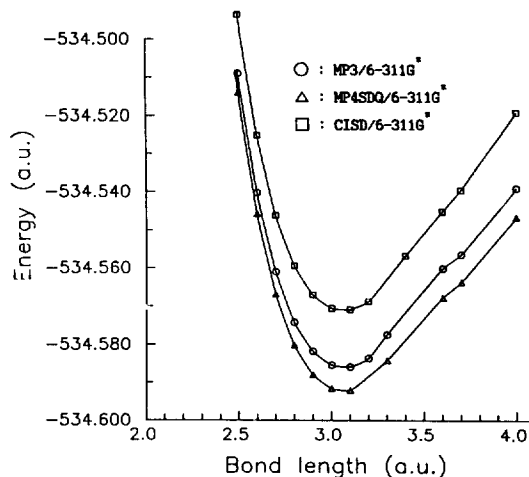
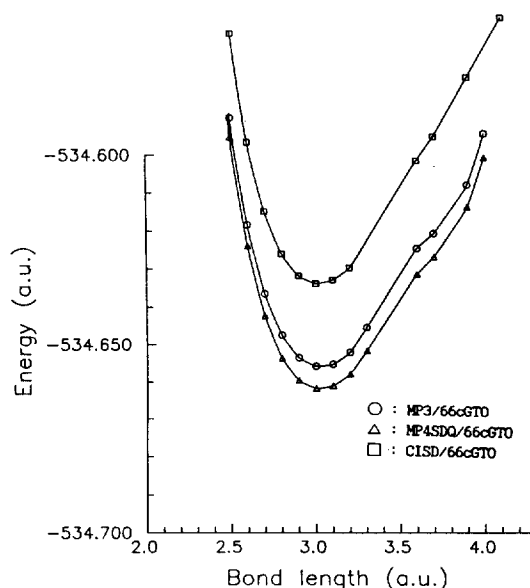
^a Atomic units.

of ClO molecule are well known, the same calculations of ClO molecule were carried out and the results were compared with experimental data. From these results of ClO it is possible to predict the range of errors in the values of various methods of calculations on ClO⁺.

ClO. For ClO radical both the experimental²⁻¹¹ and theoretical data^{21,22} are available. The various levels of the approximation method were also applied for the calculations, using the basis sets of 6-31G*, 6-311G* and 66cGTO. The total energies of the MP and CI calculations are shown in Figure 3 and 4, and their potential functions are in Table 4. The spectroscopic constants were calculated with same method used for ClO⁺, and are shown in Table 5.

The bond lengths are longer than the experimental value for all methods of calculation. But, the bond length predicted by the basis set of 66cGTO is the closest to the experimental value among the various levels of calculation. In all cases the bond lengths were decreased about 0.02 Å with the basis set of 66cGTO, and consequently those values approach to the experimental value more closely. The SCF bond length shortens by 0.02 Å upon correlation to MP3 and MP4DQ level.

For all methods using 6-31G* basis set the vibration-rotation interaction constants, α_e , are much smaller than the ex-

**Figure 3.** The potential curve of ClO with 6-311G* basis set.**Figure 4.** The potential curve of ClO with 66cGTO basis set.**Table 3.** The Calculated Spectroscopic Constants of ClO⁺

Method	Basis set	V_0 (a.u.)	R_e (Å)	α_e (MHz)	D_e (KHz)	B_e (GHz)	ω_e (cm ⁻¹)
SCF	6-31G*	-533.84676	1.4841	295	38	20.90725	1031.5
	6-311G*	-533.88580	1.4784	314	42	21.06710	993.2
	66cGTO	-533.91657	1.4661	321	47	21.42283	960.3
MP3	6-31G*	-534.13759	1.4742	134	26	21.18996	1264.3
	6-311G*	-534.19723	1.4644	161	31	21.47416	1196.8
	66cGTO	-534.26483	1.4606	149	31	21.58651	1204.9
MP4DQ	6-31G*	-534.13927	1.4738	140	27	21.19960	1259.6
	6-311G*	-534.19855	1.4640	167	31	21.48596	1193.1
	66cGTO	-534.26446	1.4572	165	34	21.68541	1155.2
MP4SDQ	6-31G*	-534.14774	1.4875	101	25	20.81072	1267.8
	6-311G*	-534.20823	1.4776	119	28	21.09223	1218.4
	66cGTO	-534.27445	1.4700	123	31	21.31074	1178.2
CISD	6-31G*	-534.12750	1.4892	141	28	20.76416	1199.4
	6-311G*	-534.18627	1.4777	164	32	21.08819	1149.7
	66cGTO	-534.24742	1.4671	166	35	21.39299	1115.5

Table 4. The Potential Energy Function^a of ClO

	Basis set	MP3	MP4DQ	MP4SDQ	CISD
V_0 (a.u.)	6-31G*	-534.52477	-534.52616	-534.53072	-534.51083
	6-311G*	-534.58470	-534.58594	-534.59107	-534.57078
	66cGTO	-534.65515	-534.65528	-534.66119	-534.63360
R_e (Å)	6-31G*	1.60842	1.60882	1.61215	1.61479
	6-311G*	1.60725	1.60782	1.61056	1.61204
	66cGTO	1.58623	1.58506	1.58698	1.59015
f^2	6-31G*	0.347779	0.338737	0.334696	0.292768
	6-311G*	0.246195	0.242699	0.242827	0.263489
	66cGTO	0.290437	0.287197	0.290226	0.291553
f^3	6-31G*	-0.643851	-0.654212	-0.607065	-0.712936
	6-311G*	-0.743493	-0.735135	-0.743564	-0.768710
	66cGTO	-0.883791	-0.881686	-0.909525	-0.813813
f^4	6-31G*	0.066199	0.069009	0.472128	0.840000
	6-311G*	1.20219	1.27600	1.35496	0.621298
	66cGTO	2.65744	2.71932	2.77999	2.74234
f^5	6-31G*	-13.1466	-12.7572	-13.8427	-10.4063
	6-311G*	-8.55671	-8.65944	-8.58039	-6.84741
	66cGTO	-11.0389	-11.0847	-10.6135	-11.6658
f^6	6-31G*	46.4210	46.0008	35.3628	42.4243
	6-311G*	39.2387	38.1906	36.5317	55.9422
	66cGTO	26.2488	25.6750	23.5201	25.7362

^a Atomic units.**Table 5.** The Calculated Spectroscopic Constants of ClO

Method	Basis set	V_0 (a.u.)	R_e (Å)	α_e (MHz)	D_e (KHz)	B_e (GHz)	ω_e (cm ⁻¹)
SCF	6-31G*	-534.23176	1.6220	307	44	17.50277	738
	6-311G*	-534.27301	1.6310	48	34	17.31070	826
	66cGTO	-534.29668	1.6083	67	33	17.80199	863
MP3	6-31G*	-534.52477	1.6084	61	30	17.79988	915
	6-311G*	-534.58470	1.6072	170	43	17.82581	770
	66cGTO	-534.65515	1.5862	164	39	18.30143	836
MP4DQ	6-31G*	-534.52616	1.6088	67	31	17.79096	903
	6-311G*	-534.58594	1.6078	172	43	17.81323	764
	66cGTO	-534.65528	1.5851	167	40	18.32841	832
MP4SDQ	6-31G*	-534.53072	1.6121	59	31	17.71767	898
	6-311G*	-534.59107	1.6106	174	43	17.75263	765
	66cGTO	-534.66119	1.5869	171	39	18.28407	836
CISD	6-31G*	-534.51083	1.6148	110	35	17.65973	840
	6-311G*	-534.57078	1.6120	155	39	17.72001	796
	66cGTO	-534.66360	1.5901	142	38	18.21125	838
exp. ^a		1.570	174	39	18.60216	854	

^aReferences 9 and 32.

perimental value while the MP3, MP4DQ and MP4SDQ values using 6-311G* and 66cGTO basis sets are close to the experimental value. The centrifugal distortion constants, D_e , are all in reasonable agreement with the experimental values. The harmonic frequencies of the MP3, MP4DQ, and MP4SDQ with 6-31G* are overestimated by about 5% and underestimated by the same amount with 6-311G* basis set, but estimated correctly by all methods with 66cGTO. The CI harmonic frequencies approach closely to experimental

values.

Discussion

Various potential energy functions have been calculated by different orders of Møller-Plesset perturbation theory and by the CI method for ClO and ClO⁺. From the molecular parameters of ClO, the reasonable agreement with experimental value was found in the calculations with 66cGTO

basis set. In bond lengths the deviation of less than 1% is good agreement. Specially the MP3 and MP4DQ calculations with the 66 cGTO basis set gave good agreements over all spectroscopic parameters. The values from CI calculations are no better than the MP values, which is different result from our previous calculations. But the MP3 calculation gave reasonably good results as usual. The previous theoretical values²² also showed longer bond lengths. But the values of α_e and D_e gave good agreement with experimental values.

In all MP levels of calculation the bigger basis set gave better results, which was expected from the previous calculations³¹.

Therefore the spectroscopic parameters of ClO^+ calculated from the method including electron correlation with large basis set will give the least discrepancies from the experimental values.

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