

Potential curves and spectroscopic properties for the ground state of ClO and for the ground and various excited states of ClO⁻

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The potential curves and dissociation energies for the ground states of ClO(²Π) and ClO⁻(¹Σ⁺) and possible low lying excited states (¹Π, ³Π, ³Σ⁻, ³Σ⁺, ¹Δ, etc.) of ClO⁻ have been investigated using sophisticated *ab initio* quantum mechanical techniques with large basis sets including diffuse functions. The equilibrium bond distance and vibrational frequency for the ground state (¹Σ⁺) of ClO⁻ are predicted to be 1.688 Å and 660 cm⁻¹ at the coupled-cluster single double (triple) [CCSD(T)]/aug-cc-pVQZ level of theory. The lowest excited singlet state of ClO⁻ is predicted to be the open-shell ¹Π state, which is 2.43 eV higher in energy than the ground state, while the lowest triplet state (³Π) of ClO⁻ has a potential with well depth of 0.32 eV. The adiabatic electron detachment energy from ClO⁻ is predicted to be 2.29 eV including zero-point vibrational energy (ZPVE) at the CCSD(T)/aug-cc-pVQZ level of theory. The spin allowed vertical electronic transition (¹Σ⁺ - ¹Π) of ClO⁻ is predicted to be 3.13 eV including ZPVE. The dissociation energies (*D*₀) of ClO⁻ to Cl⁻(¹S) + O(³P), Cl⁻(¹S) + O(¹D), and Cl(²P) + O⁻(²P) are predicted to be 1.40, 3.46, and 3.61 eV, respectively, including ZPVE. © 2002 American Institute of Physics. [DOI: 10.1063/1.1516803]

I. INTRODUCTION

The ClO radical plays an important role in the catalytic chain reaction leading to the destruction of ozone (O₃) in the stratosphere.¹ Because of the environmental importance of the ozone problem, enormous experimental and theoretical investigations have been performed on the spectroscopic properties and photochemical reactions of the ClO radical.²⁻¹⁰ On the other hand, the hypochlorite ion (ClO⁻), which is familiar in solution chemistry, has been poorly characterized in the gas phase.

The electron affinity of ClO was measured by Vogt *et al.*¹¹ in 1977 to be greater than 1.6 ± 0.2 eV from the ion-molecule reactions of Cl⁻ with O₂. In 1978, Dotan *et al.* estimated this value to be 1.95 ± 0.25 eV from the charge-exchange reactions of ClO⁻ with NO₂, SO₂, and O₃.¹² Experimental appearance potentials of ClO⁻ were reported by Dibeler *et al.* from electron impact studies on ClO₃F.¹³ The photodestruction spectra of ClO⁻ were observed by Lee *et al.* in 1979, and they attributed a broad band near 5700 Å (2.17 eV) to the photodetachment of ClO⁻ and a narrow band peaked near 4300 Å (2.88 eV) to photodissociation of ClO⁻ to Cl⁻(¹S) + O(¹D) or Cl⁻(¹S) + O(³P).¹⁴ More recently, the photoelectron spectrum of ClO⁻ in the gas phase has been observed by Gilles *et al.*, and the electron affinity of ClO, the vibrational frequency, and bond distance of ClO⁻ were determined to be 2.276 eV, 665 cm⁻¹, 1.673 Å,

respectively.¹⁵ The reaction path toward Cl + O⁻ by femto-second ultraviolet photolysis of ClO⁻ in water was reported by Lim *et al.* in 1997.¹⁶ In 2000, Distelrath and Boesl reported the electron affinity of 2.278 eV measured by the anion-zero kinetic energy (ZEKE)-photoelectron spectrum.¹⁷

A few theoretical investigations of ClO⁻ have been reported on the electron affinity, vibrational frequency, and bond distance.^{18,19} In 1971, the binding energy, vertical electron affinity, and ionization potential of ClO were predicted to be more than 2.9, 2.2 ± 0.5, and 11.2 ± 0.4 eV, respectively, by O'Hare and Wahl¹⁸ at the single configuration self-consistent field (SCF) level of theory. In 1990, the electron affinity of ClO, the equilibrium bond length, and the vibrational frequency of ClO⁻ in its ground state were estimated to be 2.16 eV, 1.694 Å and 659 cm⁻¹, respectively, based on calculations at the SDQ-MP4, CISD, CEPA levels by Peterson and Woods.¹⁹

The above-mentioned experimental observations and theoretical predictions for the electronic structure and the spectroscopic properties of ClO⁻ have focused on the ground state. The experimental observation of 2.9 eV with a width of 0.3 eV by the photodestruction cross section of ClO⁻ has not yet been clearly explained because there have not been intensive theoretical investigations on the potential curves of its excited states.¹⁴ The only theoretical study for the excited states of ClO⁻ in water is the prediction of the potential curve at the CIS level of theory by Lim *et al.*¹⁶ In the present study, we report the optimized bond distances and vibrational frequencies for the ground state (¹Σ⁺) and the

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lowest singlet ($^1\Pi$) and triplet ($^3\Pi$) excited states of ClO^- using *ab initio* quantum mechanical methods with large basis sets including diffuse functions. In addition, the electron detachment energy of ClO^- , the vertical transition energies from the ground state to various excited states of ClO^- , and the dissociation energies to the possible $\text{Cl}^- + \text{O}$ and $\text{Cl} + \text{O}^-$ fragments are examined and compared with available experimental results.

II. THEORETICAL APPROACH

The basis sets used in this study were double- ζ plus polarization functions (DZP), triple- ζ plus two sets of polarization functions (TZ2P), TZ2P basis augmented with an additional set of $10f$ functions (TZ2P+ f), DZP plus diffuse functions (DZP+diff), TZ2P plus diffuse functions (TZ2P+diff), and TZ2P+ f plus diffuse functions (TZ2P+ f +diff). The DZP basis set consisted of the standard Huzinaga and Dunning double- ζ set of contracted Gaussian functions ($9s5p$ primitive set for oxygen^{20,21} and $11s7p$ primitive set for chlorine²²) augmented with a single set of polarization $6d$ functions on chlorine and oxygen, with orbital exponents $\alpha_d(\text{Cl})=0.75$, and $\alpha_d(\text{O})=0.85$. The TZ2P basis consists of McLean and Chandler's²³ contraction of Huzinaga's $12s9p$ basis for chlorine and Dunning's contraction of Huzinaga's $10s6p$ set for oxygen with two sets of polarization functions with exponents $\alpha_d(\text{Cl})=1.5$, 0.375 , and $\alpha_d(\text{O})=1.7$, 0.425 . The TZ2P+ f basis set was formed by adding a set of $10f$ functions with orbital exponents $\alpha_f(\text{Cl})=0.7$, and $\alpha_f(\text{O})=1.4$. The DZP+diff, TZ2P+diff, and TZ2P+ f +diff basis sets were constructed by adding one set of s and p diffuse functions on Cl and O to the DZP, TZ2P, and TZ2P+ f basis sets. The exponents of the diffuse functions were determined in the manner described in Lee and Schaefer's paper,²⁴ and they are $\alpha_s(\text{Cl})=0.05048$ and $\alpha_p(\text{Cl})=0.05087$, $\alpha_s(\text{O})=0.08227$ and $\alpha_p(\text{O})=0.06508$ for the DZP+diff basis set, and $\alpha_s(\text{Cl})=0.05541$ and $\alpha_p(\text{Cl})=0.04531$, $\alpha_s(\text{O})=0.08993$, and $\alpha_p(\text{O})=0.05840$ for the TZ2P+diff and TZ2P+ f +diff basis sets. Since these basis sets were not efficacious for coupled-cluster single double (triple) [CCSD(T)] and CCSDT calculations on the dissociation energies (see Table V), we employed Dunning *augmented* correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ), quadruple-zeta (aug-cc-pVQZ), quintuple-zeta (aug-cc-pV5Z), and sextuple-zeta (aug-cc-pV6Z) basis sets.²⁵ The appropriate set of spherical harmonic ($5d$, $7f$, $9g$, etc.) basis functions was used for the aug-cc-pVXZ basis sets.

The geometries of the ground states of ClO ($^2\Pi$) and ClO^- ($^1\Sigma^+$), and the excited states ($^1\Pi$, $^3\Pi$) of ClO^- were fully optimized at the self-consistent field (SCF) level of theory using analytic gradient techniques²⁶ with all basis sets employed in this investigation. All open-shell SCF calculations were carried out using restricted open-shell Hartree-Fock (ROHF) orbitals. For the ground state ($^1\Sigma^+$) of ClO^- , geometries were optimized at the CCSD and CCSD(T) levels.²⁷ In the CCSD and CCSD(T) energy calculations with all basis sets except aug-cc-pVXZ, the six core-like occupied

SCF molecular orbitals were frozen (held doubly occupied) and the six highest virtual molecular orbitals were deleted from the correlation procedures.

Spin-unrestricted Hartree-Fock (UHF) CCSD and CCSD(T) were applied to the ground state ($^2\Pi$) of ClO and the $^3\Pi$ state of ClO^- .²⁸ For the open-shell excited states of ClO^- , geometry optimizations and vertical transition energy calculations were carried out using equation-of-motion excited state (EOMEE) and the quasi-restricted Hartree-Fock (QRHF) two-determinant (TD) coupled cluster (CC) methods.^{29,30} For more precise computations on dissociation energies of ClO^- , the single point energies were obtained at the CCSDT³¹ level of theory with the aug-cc-pVXZ basis set by freezing core electrons, one for O and five for Cl, respectively.

For the best prediction of dissociation limits of ClO^- to possible Cl and O fragments, UHF energies for each Cl, Cl^- , O (3P and 1D states), and O^- species were extrapolated to the aug-cc-pVXZ basis limit using a three-parameter exponential function of the form^{25,32}

$$E_X = E_\infty + A e^{-BX},$$

where X represents the cardinal number of the aug-cc-pVXZ basis set (for example, aug-cc-pVTZ, $X=3$). The CCSD, CCSD(T), and CCSDT correlation energies were each fit to a two-parameter function of the form³³

$$E_X = E_\infty + A/X^3.$$

For both cases, the atomic energies used for the extrapolations were computed using the aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, and aug-cc-pV6Z basis sets. However, aug-cc-pV5Z and aug-cc-pV6Z basis sets were too large for ClO^- ; therefore the dissociation energies from the ground state of ClO^- to Cl^- (1S) + O (3P) fragments were computed at the CCSDT/aug-cc-pVQZ level of theory using the optimized geometry at the CCSD(T)/aug-cc-pVQZ level and extrapolated to the basis limit. The dissociation energies of ClO^- to other fragments were predicted using the relative energies between Cl and O fragments obtained from the extrapolation scheme mentioned above.

Harmonic and fundamental vibrational frequencies for the ground states of ClO and ClO^- were evaluated using analytic second energy derivatives at the SCF level and using finite differences of analytic gradients at the CCSD, and CCSD(T) levels with all employed basis sets except the aug-cc-pVXZ sets.^{34,35} Analytic second derivatives were used for harmonic frequencies at the CCSD and CCSD(T) levels with the aug-cc-pVTZ and aug-cc-pVQZ basis sets, and fundamental frequencies were computed using finite differences of analytic second derivatives at the same levels of theory.³⁶ The vertical transition energies to various excited states of ClO^- and the ground state of ClO were obtained at the optimized geometry of the ground state of ClO^- and used to estimate the electron affinity of ClO with zero-point vibrational energy (ZPVE) corrections. All computations except coupled cluster calculations with the aug-cc-pVXZ basis set were carried out with the PSI-2³⁷ suite of programs and EOM-

TABLE I. Absolute energies, bond distances, harmonic (ω) and fundamental (ν) vibrational frequencies, and ZPVEs for the ground state (${}^1\Sigma^+$) of ClO^- at various levels of theory.

	E (hartree)	R (Å)	ω (cm^{-1})	ν (cm^{-1})	ZPVE (eV)
DZP SCF	-534.264 939	1.740	578	567	0.036
DZP+diff SCF	-534.284 223	1.721	591	579	0.036
TZ2P SCF	-534.323 778	1.717	600	588	0.037
TZ2P+diff SCF	-534.330 064	1.705	612	601	0.038
TZ2P+ f SCF	-534.329 283	1.686	631	618	0.039
TZ2P+ f +diff SCF	-534.335 484	1.675	646	633	0.040
DZP CCSD	-534.681 040	1.743	646	638	0.040
DZP+diff CCSD	-534.711 937	1.735	640	632	0.040
TZ2P CCSD	-534.799 261	1.740	635	628	0.039
TZ2P+diff CCSD	-534.809 158	1.733	638	632	0.039
TZ2P+ f CCSD	-534.866 647	1.704	664	656	0.041
TZ2P+ f +diff CCSD	-534.875 901	1.700	669	661	0.041
aug-cc-pVTZ CCSD	-534.854 192	1.690	685	677	0.042
aug-cc-pVQZ CCSD	-534.938 946	1.674	694	686	0.043
DZP CCSD(T)	-534.689 993	1.758	614	606	0.038
DZP+diff CCSD(T)	-534.722 861	1.753	601	593	0.037
TZ2P CCSD(T)	-534.815 786	1.754	611	604	0.038
TZ2P+diff CCSD(T)	-534.826 557	1.748	612	605	0.038
TZ2P+ f CCSD(T)	-534.887 169	1.718	640	632	0.040
TZ2P+ f +diff CCSD(T)	-534.897 184	1.711	642	634	0.040
aug-cc-pVTZ CCSD(T)	-534.877 489	1.704	658	650	0.041
aug-cc-pVQZ CCSD(T)	-534.965 123	1.688	669	660	0.041
Experiment		1.71 ^a	713 ^a		
		1.673 ^b	665±25 ^b		

^aReference 14.^bReference 15.

CC, QRHF-CC, and other coupled cluster calculations with the aug-cc-pVXZ basis set were carried out using the ACES II package of quantum chemical programs.³⁸

III. RESULTS AND DISCUSSION

A. The ${}^1\Sigma^+$ ground state of ClO^-

The electronic configuration and molecular term symbol for the ground state of ClO^- are

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^4 \Rightarrow {}^1\Sigma^+.$$

The optimized geometries and absolute energies for the ground state of ClO^- at various levels of theory are shown in Table I. In general, bond lengths decrease with increasing basis set sizes for all methods employed. At the CCSD and CCSD(T) levels of theory, the basis set effects in going from DZP to TZ2P are not very significant, while the effects of f functions are relatively important. For example, bond distances decrease by 0.004 Å or less in going from DZP to TZ2P but they decrease by 0.036 Å from TZ2P to TZ2P+ f at both the CCSD and CCSD(T) levels of theory. The effects of diffuse functions (one s and one set of p functions) are less important with large basis set such as TZ2P+ f . The electron correlation effects with the TZ2P+ f +diff basis set increase the ClO^- bond distance by 0.025 Å in going from SCF to CCSD and by 0.011 Å from CCSD to CCSD(T). At the highest level of theory employed in this investigation, CCSD(T)/aug-cc-pVQZ, the bond distance is predicted to be 1.688 Å, which is in between the early experimental results of 1.71 Å¹⁴ and 1.673 Å.¹⁵

The harmonic and fundamental vibrational frequencies and ZPVEs for the ground state of ClO^- are also presented in Table I. The addition of f functions increases the vibrational frequencies significantly at all levels of theory, which is consistent with the above-described bond distance shortening. The predicted vibrational frequency of 660 cm^{-1} at the CCSD(T)/aug-cc-pVQZ level of theory is in very good agreement with the experimental value of 665±25 cm^{-1} by Gilles in 1992.¹⁵

B. The ${}^2\Pi$ ground state of ClO

The electronic structure and spectroscopic properties of the ClO radical have been well characterized by both experimental and theoretical investigations. The electronic configuration and molecular term symbol for the ground state of ClO are

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^3 \Rightarrow {}^2\Pi$$

and the absolute and relative energies, optimized bond distances, and vibrational frequencies of the ground state (${}^2\Pi$) of ClO at various levels of theory are listed in Table II. Diffuse functions have significant effects on the relative energies, and the f functions are important for the optimized bond lengths. The predicted bond distance and fundamental vibrational frequency of 1.576 Å and 850 cm^{-1} at the CCSD(T)/aug-cc-pVQZ level of theory are in good agreement with experimental results of 1.570 Å and 854 cm^{-1} .^{39,40} From the relative energies and the vibrational frequencies of ClO, the adiabatic electron affinity is predicted to be 2.28 eV without ZPVE correction and 2.29 eV including ZPVE at the

TABLE II. Relative (in eV) energies for the lowest singlet ($^1\Pi$) and triplet ($^3\Pi$) excited states of ClO^- and the ground state ($^2\Pi$) of ClO , and harmonic (ω) and fundamental (ν) vibrational frequencies (in cm^{-1}) and ZPVE (in eV) of ClO .

	$^2\Pi$ state (ClO)					$^1\Pi$ state (ClO^-) ^a		$^3\Pi$ state (ClO^-)	
	Energy (ΔE) ^b	R (\AA)	ω	ν	ZPVE	Energy (ΔE) ^b	R (\AA)	Energy (ΔE) ^b	R (\AA)
DZP SCF	0.54	1.613	832	811	0.051	1.00	2.704	-1.19	3.099
DZP+diff SCF	0.98	1.611	833	812	0.051	0.77	3.261	-1.45	3.503
TZ2P SCF	0.80	1.611	811	793	0.050	0.92	3.083	-1.29	3.348
TZ2P+diff SCF	0.94	1.610	811	794	0.050	0.90	3.245	-1.32	3.473
TZ2P+f SCF	0.75	1.593	835	821	0.052	0.99	3.137	-1.18	3.368
TZ2P+f+diff SCF	0.89	1.592	837	823	0.052	0.98	3.272	-1.19	3.479
DZP CCSD	1.21	1.618	819	809	0.051	2.10	2.292	0.55	2.423
DZP+diff CCSD	1.87	1.616	817	807	0.051	2.13	2.255	0.47	2.510
TZ2P CCSD	1.81	1.614	796	787	0.049	2.16	2.266	0.50	2.484
TZ2P+diff CCSD	2.03	1.612	796	787	0.049	2.18	2.239	0.53	2.501
TZ2P+f CCSD	1.83	1.587	840	830	0.052	2.29	2.251	0.68	2.457
TZ2P+f+diff CCSD	2.03	1.586	843	833	0.052	2.32 (2.35)	2.222 (2.148)	0.73	2.461
aug-cc-pVTZ CCSD	2.13	1.582	859	849	0.053	2.39 (2.42)	2.209 (2.117)	0.81	2.444
aug-cc-pVQZ CCSD	2.18	1.570	874	864	0.054	2.44 (2.43)	2.215 (2.081)	0.86	2.453
aug-cc-pVTZ CCSD(T)	2.23	1.589	845	835	0.052			0.98	2.377
aug-cc-pVQZ CCSD(T)	2.28	1.576	861	850	0.053			1.04	2.379
Experiment	2.276 ^c	1.570 ^d		854 ^e					

^aThe geometry optimizations for the $^1\Pi$ state of ClO^- at the CCSD level of theory were carried out using the EOM-CCSD method, while the values in parentheses were obtained using QRHF-based TD-CCSD.

^bRelative to the ground state ($^1\Sigma^+$) of ClO^- .

^cReference 15.

^dReference 39.

^eReference 40.

CCSD(T)/aug-cc-pVQZ level of theory. The experimental electron affinities of ClO were reported to be 1.95 ± 0.25 eV by Dotan *et al.*,¹² less than 2.17 eV by Lee *et al.*,¹⁴ 2.276 eV by Gilles *et al.*,¹⁵ and 2.278 eV by Distelrath and Boesl.¹⁷ Our prediction is in very good agreement with the more recent experimental results.

C. The lowest singlet and triplet excited states of ClO^- : $^1\Pi$, $^3\Pi$

The following electronic configuration and molecular term symbols are for the lowest singlet and triplet excited states of ClO^- :

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^3 8\sigma \Rightarrow ^1\Pi, ^3\Pi.$$

Relative energies and bond distances for the lowest $^1\Pi$ and $^3\Pi$ excited states of ClO^- at various levels of theory are presented in Table II. For the lowest open-shell singlet, $^1\Pi$, state of ClO^- , CCSD geometry optimizations were carried out using EOM-CC and QRHF-based TD-CC methods.

It is well known that a single-reference Hartree-Fock wave function does not adequately describe the open-shell singlet ($^1\Pi$) and triplet ($^3\Pi$) excited states of ClO^- , and correlation effects are very important. For the $^3\Pi$ state, the f function effect is more significant than the effect of diffuse functions. The relative energy increases by 0.18 eV and the bond distance decreases by 0.074 \AA in going from CCSD to CCSD(T) with the aug-cc-pVQZ basis set. At the highest level employed in the present research, the relative energies and bond distances are predicted to be 2.43 eV and 2.081 \AA for the $^1\Pi$ state of ClO^- and 1.04 eV and 2.379 \AA for the $^3\Pi$ state. In the previous theoretical study, Lim *et al.* reported that the lowest $^1\Pi$ state is a dissociative potential based on

the CIS level calculations but they mentioned that more reliable excited state potentials of ClO^- are required at higher level of theory.¹⁶

D. Vertical transition energies

The vertical electronic transition energies from the ground state of ClO^- to the $^2\Pi$ state of ClO and the lowest singlet ($^1\Pi$) and triplet ($^3\Pi$) excited states of ClO^- are reported in Table III. The vertical detachment energy is predicted to be 2.39 eV including ZPVE at the CCSD(T)/aug-cc-pVQZ level of theory, which is slightly higher than the experimental observation of 2.17 eV by Lee *et al.* in 1979.¹⁴ However the recent experimental observations of 2.278 eV for the adiabatic electron affinity imply that the vertical electron detachment should be larger than 2.278 eV. The vertical electronic transition energies are predicted to be 3.07 eV for the lowest triplet state ($^3\Pi$) and 3.17 eV for the lowest singlet excited state ($^1\Pi$) at the aug-cc-pVTZ CCSD(T) level of theory without ZPVE corrections. The $^1\Sigma^+ - ^3\Pi$ transition is spin forbidden, but the experimental observation for the spin allowed $^1\Sigma^+ - ^1\Pi$ transition was reported to be 2.9 ± 0.3 eV by Lee *et al.*¹⁴ Our best prediction of 3.13 eV including ZPVE is within the error bar of this experimental result.

Some other possible low lying singlet and triplet excited states of ClO^- have been also examined using CCSD and CCSD(T) methods with DZP+diff, TZ2P+diff, TZ2P+f+diff, and aug-cc-pVTZ basis sets. The electronic configurations and molecular term symbols for these excited states are as follows:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^3 9\sigma \Rightarrow ^1\Pi, ^3\Pi,$$

TABLE III. Relative (in eV) energies for the vertical transitions from the ground state ($^1\Sigma^+$) of ClO^- to the $^2\Pi$ state of ClO , and the $^1\Pi$ and $^3\Pi$ states of ClO^- at various levels of theory.

	$^2\Pi$ state (ClO)	$^1\Pi$ state (ClO^-) ^a	$^3\Pi$ state (ClO^-)
DZP SCF	0.89	2.85	1.73
DZP+diff SCF	1.28	2.61	1.71
TZ2P SCF	1.10	2.86	1.87
TZ2P+diff SCF	1.22	2.65	1.87
TZ2P+f SCF	1.04	3.13	2.20
TZ2P+f+diff SCF	1.16	2.80	2.14
DZP CCSD	1.38	3.57 (3.58)	2.44
DZP+diff CCSD	2.02	3.04 (2.99)	2.26
TZ2P CCSD	1.98	3.35 (3.34)	2.34
TZ2P+diff CCSD	2.19	3.05 (2.92)	2.27
TZ2P+f CCSD	1.99	3.58 (3.57)	2.65
TZ2P+f+diff CCSD	2.19	3.21 (3.06)	2.51
aug-cc-pVTZ CCSD	2.27	3.23 (3.09)	2.57
aug-cc-pVQZ CCSD	2.32	3.27 (3.08)	2.63
DZP CCSD(T)	1.38	2.89	2.35
DZP+diff CCSD(T)	2.07	2.71	2.43
TZ2P CCSD(T)	2.04	2.73	2.25
TZ2P+diff CCSD(T)	2.26	2.86	2.63
TZ2P+f CCSD(T)	2.05	2.99	2.55
TZ2P+f+diff CCSD(T)	2.27	3.03	2.82
aug-cc-pVTZ CCSD(T)	2.38	3.11	2.90
aug-cc-pVQZ CCSD(T)	2.43	3.17	3.07
Experiment ^b	2.17	2.90	...

^aThe single-point energies for the $^1\Pi$ state of ClO^- at the CCSD level of theory were carried out using the EOM-CCSD method, while the values in parentheses and the CCSD(T) results were obtained using a two-determinant QRHF reference.

^bReference 14.

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^3 4\pi \\ \Rightarrow ^3\Sigma^+, ^3\Sigma^-, ^3\Delta, ^1\Sigma^+, ^1\Sigma^-, ^1\Delta.$$

These excited states were identified using equation-of-motion excited state (EOMEE) and the quasi-restricted Hartree–Fock (QRHF) two-determinant (TD) coupled cluster (CC) methods. The vertical electron transition energies from the ground state to various excited states of ClO^- are

listed in Table IV. The second triplet (T_2) and singlet (S_2) excited states come from an electron transition of 3π to 9σ to result the $^3\Pi$ and $^1\Pi$ states. The other excited states arise from an electron transition of 3π to 4π .

E. Dissociation energies to the $\text{Cl}+\text{O}^-$ and Cl^-+O fragments

Among the possible fragments of the dissociation process of ClO^- , the $\text{Cl}^-(^1S)+\text{O}(^3P)$ fragments should be readily accessible from the triplet excited states, $^3\Pi$ or $^3\Sigma^-$. The $\text{Cl}^-(^1S)+\text{O}(^1D)$ and $\text{Cl}(^2P)+\text{O}^-(^2P)$ limits will be accessible from the ground state ($^1\Sigma^+$) or the lowest singlet state ($^1\Pi$) by spin conservation. The dissociation limits to these fragments at various levels of theory are presented in Table V. The dissociation limit to $\text{Cl}(^2P)+\text{O}^-(^2P)$ is predicted to lie below the dissociation limit to $\text{Cl}^-(^1S)+\text{O}(^1D)$ at relatively low levels (SCF and CCSD) of theory but the dissociation process to $\text{Cl}^-(^1S)+\text{O}(^1D)$ is energetically favorable at higher levels of theory like CCSDT with large basis sets. Single-point CCSDT energies were obtained at the geometry optimized at the CCSD(T) level of theory and used to extrapolate to the basis set limit, namely, aug-cc-pV ∞ Z CCSDT.

The absolute and relative energies of ClO^- and dissociation limits at the CCSD, CCSD(T), and CCSDT levels with the aug-cc-pVXZ basis set are listed in Table VI. The energies for individual fragments of Cl and O have been computed up to the aug-cc-pV6Z CCSDT level of theory and extrapolated to basis set limit by the method mentioned in Sec. II. At the aug-cc-pV ∞ Z CCSDT level, the dissociation limits to $\text{Cl}^-(^1S)+\text{O}(^1D)$ and $\text{Cl}(^2P)+\text{O}^-(^2P)$ are predicted to be 3.46 and 3.61 eV, respectively, including a ZPVE of 0.04 eV from the aug-cc-pVQZ CCSD(T) level of theory. This result can be favorably compared with experimental estimation [3.46 eV for D_0 of ClO^- to $\text{Cl}(^2P)+\text{O}^-(^2P)$ dissociation limit] of Lee *et al.*¹⁴ The predicted dissociation limit (1.40 eV including ZPVE) of ClO^- to $\text{Cl}^-(^1S)+\text{O}(^3P)$ at the aug-cc-pV ∞ Z CCSDT level of

TABLE IV. Relative (in eV) energies for the vertical transitions of ClO^- from the ground state to various possible excited states at the optimized geometries of the ground state ($^1\Sigma^+$).

	CCSD ^a				CCSD(T)			
	DZP+diff	TZ2P+diff	TZ2P+f+diff	aug-cc-pVTZ	DZP+diff	TZ2P+diff	TZ2P+f+diff	aug-cc-pVTZ
$X(^1\Sigma^+)$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$T_1(^3\Pi)$	2.17 (2.26)	2.22 (2.27)	2.49 (2.51)	2.54 (2.57)	2.43	2.63	2.81	2.90
$S_1(^1\Pi)$	3.04 (3.00)	3.05 (2.93)	3.21 (3.08)	3.23 (3.09)	2.73	2.88	3.05	3.11
$T_2(^3\Pi)$	4.40	4.53	4.50	4.81
$S_2(^1\Pi)$	4.52	4.63	4.61	4.93
$T_3(^3\Sigma^+)$	5.67 (5.82)	5.18 (5.26)	5.10 (5.16)	5.00 (5.06)	5.83	5.27	5.18	5.10
$T_4(^3\Delta)$	5.85 (5.96)	5.31 (5.36)	5.23 (5.25)	5.12 (5.15)	5.97	5.37	5.27	5.19
$S_3(^1\Delta)$	5.90 (5.97)	5.34 (5.37)	5.26 (5.26)	5.15 (5.16)	5.98	5.37	5.28	5.19

^aThe single-point energies at the CCSD level of theory were carried out using the EOM-CCSD method, while the values in parentheses and the CCSD(T) results were obtained using a two-determinant QRHF reference.

TABLE V. Dissociation (in eV) energies of ClO^- to $\text{Cl}^- + \text{O}$ and $\text{Cl} + \text{O}^-$ fragments at various levels of theory.

	$\text{Cl}^-(^1S) + \text{O}(^1D)$ (eV)	$\text{Cl}(^2P) + \text{O}^-(^2P)$ (eV)	$\text{Cl}^-(^1S) + \text{O}(^3P)$ (eV)
DZP SCF	2.24	2.00	-1.07
DZP+diff SCF	1.90	1.72	-1.41
TZ2P SCF	2.10	1.97	-1.21
TZ2P+diff SCF	2.04	1.83	-1.27
TZ2P+f SCF	2.19	2.06	-1.11
TZ2P+f+diff SCF	2.16	1.94	-1.14
DZP CCSD	3.45	3.22	0.99
DZP+diff CCSD	3.18	2.83	0.71
TZ2P CCSD	3.24	3.20	0.78
TZ2P+diff CCSD	3.23	2.98	0.76
TZ2P+f CCSD	3.38	3.36	0.97
TZ2P+f+diff CCSD	3.38	3.16	0.97
aug-cc-pVTZ CCSD	3.41	3.24	1.01
DZP CCSD(T)	3.43	3.37	1.15
DZP+diff CCSD(T)	3.16	2.97	0.87
TZ2P CCSD(T)	3.30	3.39	1.03
TZ2P+diff CCSD(T)	3.29	3.16	1.02
TZ2P+f CCSD(T)	3.44	3.57	1.22
TZ2P+f+diff CCSD(T)	3.45	3.34	1.23
aug-cc-pVTZ CCSD(T)	3.47	3.44	1.26
aug-cc-pVTZ CCSDT	3.36	3.41	1.25
aug-cc-pVQZ CCSDT	3.42	3.53	1.34
aug-cc-pV ∞ Z CCSDT	3.50	3.65	1.44

theory is in very good agreement with the experimental result of 1.409 eV by Gilles *et al.*¹⁵

The predicted potential curves for the ground ($^1\Sigma^+$) and lowest singlet ($^1\Pi$) and triplet ($^3\Pi$) excited states of ClO^- and the ground state ($^2\Pi$) of ClO are shown in Fig. 1. The results for the ground states of ClO and ClO^- and the asymptotic values of $\text{Cl} + \text{O}$ fragments are in reasonably good agreement with the tentative potential curves using ex-

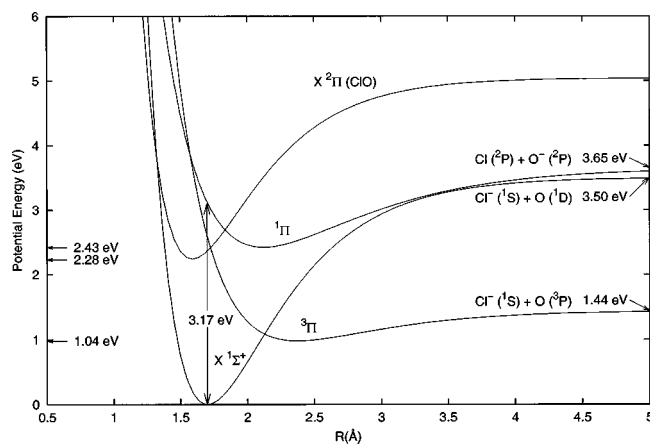


FIG. 1. Potential energy curves for the ground states of $\text{ClO}(^2\Pi)$ and $\text{ClO}^-(^1\Sigma^+)$ and lowest singlet and triplet excited states ($^1\Pi$ and $^3\Pi$) of ClO^- at the highest levels of theory employed.

perimental parameters observed and derived based on the iso-electronic and relatively well-investigated ArO potential curve.¹⁴ Because of their presumed dissociative potential curves of the lowest singlet and triplet excited states of ClO^- , however, they could not interpret adequately their observed band at peak 2.9 ± 0.3 eV. Here we can assign this peak as the $^1\Sigma^+ - ^1\Pi$ transition of ClO^- due to our prediction of the attractive potential for the lowest $^1\Pi$ state.

IV. CONCLUDING REMARKS

The spectroscopic properties and potential curves of the ground state of ClO and ClO^- , and the low lying excited states of ClO^- have been examined using high level *ab initio* quantum mechanical methods. The bond distance and vibrational frequency of the ground state ($^1\Sigma^+$) of ClO^- are predicted to be 1.688 Å and 660 cm^{-1} at the CCSD(T)/aug-cc-

TABLE VI. Absolute (in hartree) and relative (in eV) energies for ClO^- , $\text{Cl}^-(^1S) + \text{O}(^1D)$, $\text{Cl}(^2P) + \text{O}^-(^2P)$, and $\text{Cl}^-(^1S) + \text{O}(^3P)$ at the aug-cc-pVXZ CCSD, CCSD(T) and CCSDT levels of theory.

	$\text{ClO}^-(^1\Sigma^+)^a$	1 $\text{Cl}^-(^1S) + \text{O}(^1D)$	2 $\text{Cl}(^2P) + \text{O}^-(^2P)$	3 (ΔE , eV) ^b $\text{Cl}^-(^1S) + \text{O}(^3P)$	$\Delta E(1-2)$	$\Delta E(1-3)$
aug-cc-pVTZ CCSD	-534.808 039	-534.682 792	-534.689 111	-534.771 077(1.01)	-0.17	2.40
aug-cc-pVQZ CCSD	-534.847 652	-534.720 177	-534.724 451	-534.807 725(1.09)	-0.12	2.38
aug-cc-Pv5Z CCSD	...	-534.732 181	-534.735 993	-534.819 427	-0.10	2.37
aug-cc-pV6Z CCSD	...	-534.736 366	-534.740 071	-534.823 490	-0.10	2.37
aug-cc-pV ∞ Z CCSD	-534.879 831	-534.743 401	-534.746 585	-534.830 361(1.35)	-0.09	2.37
aug-cc-pVTZ CCSD(T)	-534.830 436	-534.702 992	-534.704 096	-534.783 994(1.26)	-0.03	2.20
aug-cc-pVQZ CCSD(T)	-534.872 345	-534.742 358	-534.741 419	-534.822 522(1.36)	0.03	2.18
aug-cc-Pv5Z CCSD(T)	...	-534.755 220	-534.753 787	-534.835 027	0.04	2.17
aug-cc-pV6Z CCSD(T)	...	-534.759 727	-534.758 188	-534.839 390	0.04	2.17
aug-cc-pV ∞ Z CCSD(T)	-534.900 291	-534.767 188	-534.765 129	-534.846 667(1.46)	0.06	2.16
aug-cc-pVTZ CCSDT	-534.830 723	-534.707 278	-534.705 388	-534.784 814(1.25)	0.05	2.11
aug-cc-pVQZ CCSDT	-534.872 487	-534.746 834	-534.742 618	-534.823 245(1.34)	0.12	2.08
aug-cc-Pv5Z CCSDT	...	-534.759 671	-534.754 888	-534.835 659	0.13	2.07
aug-cc-pV6Z CCSDT	...	-534.764 120	-534.759 096	-534.839 950	0.14	2.06
aug-cc-pV ∞ Z CCSDT	-534.900 326	-534.771 661	-534.766 251	-534.847 231(1.44)	0.15	2.06
Expt.				1.409 ^c	0.184 ^d	1.967 ^d

^aSingle-point energies using six frozen core orbitals. CCSDT single-point energies were obtained at the geometries optimized at the CCSD(T) level of theory. The aug-cc-pV ∞ Z CC energies were obtained by extrapolation to the basis set limit.

^bDissociation energy from the ground state of ClO^- to $\text{Cl}^-(^1S) + \text{O}(^3P)$.

^cReference 15.

^dReference 14.

pVQZ level of theory and can be compared reasonably well with the experimental results. The optimized bond distance and vibrational frequency of the ground state ($^2\Pi$) of ClO are predicted to be 1.576 Å and 850 cm^{-1} . The adiabatic electron affinity of ClO is estimated to be 2.29 eV and the vertical electron detachment energy of ClO^- is predicted to be 2.39 eV including ZPVE corrections.

The lowest excited singlet state of ClO^- is predicted to be the open shell $^1\Pi$ state and is located higher in energy by 2.43 eV at 2.081 Å than the ground state of ClO^- , while the lowest triplet state ($^3\Pi$) of ClO^- has very flat potential curve with well depth of 0.32 eV at 2.379 Å. The vertical $^1\Sigma^+ - ^1\Pi$ electronic transition is predicted to be 3.13 eV at the CCSD(T)/aug-cc-pVTZ level of theory including ZPVE correction, which is well below the dissociation limit to $\text{Cl}^-(^1S) + \text{O}(^1D)$. The dissociation energies (D_0) to $\text{Cl}^-(^1S) + \text{O}(^3P)$, $\text{Cl}^-(^1S) + \text{O}(^1D)$, and $\text{Cl}(^2P) + \text{O}^-(^2P)$ are predicted to be 1.40, 3.46, and 3.61 eV, respectively, including ZPVE, using extrapolations of CCSDT energies to the basis set limits. These predictions are expected to be accurate to within 0.1 eV in all cases, although even smaller error bars could be obtained using high-level focal point techniques.

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