Theoretical study on the ground and excited states of MnO$_4^-$

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The symmetry adapted cluster (SAC) and SAC-configuration interaction (SAC-CI) theories are applied to the calculations of the ground and excited states of MnO$_4^-$. With the use of three different active spaces, we examine the convergence of the results. Electron correlations work to relax charge polarizations of the Mn–O bonds in the ground state. The experimental spectrum of MnO$_4^-$ is well reproduced by the present calculations. All of the observed peaks are assigned to the electronic allowed transitions to the $^1T_2$ excited states. They are characterized as the excitations from the nonbonding orbitals of oxygen to the antibonding orbitals between the metal and oxygens. For reasonable descriptions of the ground and excited states of MnO$_4^-$, electron correlations should be considered with the use of large enough active space for expressing the relaxations of valence electrons. In this sense, all of the previous theoretical assignments of the spectra are unreliable, since they are not the results of calculations including sufficient amount of electron correlations.

I. INTRODUCTION

The permanganate ion MnO$_4^-$ has been extensively used as an oxidizing agent. The electronic structures of the ground and excited states of the ion have been studied both experimentally and theoretically. Since Teltow reported the visible uv spectra of MnO$_4^-$ in 1938,[1] much experimental data have been accumulated for the spectra.[1-5] On the theoretical side, Wolfsberg and Helmholtz performed a pioneering study on the electronic absorption spectra by the molecular orbital (MO) calculations.[6] Since then, $X\alpha$ (Refs. 7–9), *ab initio* Hartree Fock (HF) (Refs. 10–15), and singles and doubles configuration interaction (SD-CI) (Ref. 16) calculations have been carried out for spectral assignments. However, in these theoretical studies, the calculated excitation energies did not agree well with the experimental values and several different assignments were proposed.

Buijse et al.[17] indicated that quasidegenerate electron correlations are important for the ground state of MnO$_4^-$. They mentioned that a reason of an underestimation for the excitation energies of the first few excited states by the delta-self-consistent-field (ΔSCF) procedure lies in a larger correlation error in the ground state than in the excited states.

Recently, we have reported theoretical studies for the excited states of the metal complexes, RuO$_4$, OsO$_4$, MoO$_{4-n}$S$_n^{2-}$ ($n = 0$–4), MoSe$_4^{2-}$, and TiCl$_4$.[18-20] We used the symmetry adapted cluster[21] (SAC) and SAC-CI[22] methods, which are shown to be very useful for studying excited and ionized states of molecules.[23] We have given systematic assignments for the excited states of these molecules in good agreement with the experimental spectra.

In this study, we calculate the ground and excited states of MnO$_4^-$ by the SAC/SAC-CI method. We first investigate the electronic structure of the ground state, that is, the bonding character between metal and ligands, the ionicity of the complex, etc. We next compare the calculated spectrum of the permanganate ion with the experimental one and give our assignment of the observed peaks. We also compare our results with the previous theoretical results.

II. COMPUTATIONAL DETAILS

The geometry of the MnO$_4^-$ ion is fixed to the regular tetrahedron with the metal-oxygen bond length of 1.629 Å, the x-ray crystallographic experimental data.[24] The Gaussian basis sets used in this study are as follows. In the atomic state, the ^6D state of Mn with the electronic configuration $3d^64s^14p^0$ is higher in energy than the ^6S state with $3d^54s^24p^0$. However, the former configuration is closer to the configuration in the molecular state, so that $(14s8p5d)/[6s2p2d]$ set optimized for the ^6D state is employed for Mn. Furthermore, two p ($\zeta_p = 0.119, 0.039$) functions[25] are added for representing the $4p$ orbital, and one d ($\zeta_d = 0.1281$) function due to Rappe et al.[26] for reinforcing the $3d$ orbital. For oxygen, we use the $(9s5p)/[4s2p]$ set of Huzinaga–Dunning.[27,28] All-electron HF wave functions for the ground state is calculated by the program GAMESS.[29]

The electron correlations in the ground state are taken into account by the SAC theory[21] and those in the excited states by the SAC-CI theory.[22] The calculations are carried out with the use of the program SAC85.[30] The active space in the SAC/SAC-CI calculations consists of 12 higher occupied orbitals and 41 lower unoccupied orbitals calculated by the HF method. The 12 occupied orbitals are mainly made of the $3d$ atomic orbitals of Mn and the $2p$ atomic orbitals of O. All single-excitation operators are included in the linked term and double-excitation operators are selected by the second-order perturbation method. For the ground state, the double-excitation operators whose perturbation energy contribution is larger than 7×10^{-5} hartree are included. For excited states, the threshold of 1×10^{-4} hartree is used with respect to the main configurations ($C \geqslant 0.2$) of the ten lower single excitation (SE)-CI solutions.[31] In the SAC/SAC-CI method, the triple and quadruple excitations are considered in the unlinked terms as the products of lower excitations. The selections are performed by the method described previously.[31] Table I shows the dimensions of the SAC/SAC-CI calculations for the ground and excited states of MnO$_4^-$. By virtue of the SAC/SAC-CI formalism, the dimensions of the

TABLE I. Dimensions of the SAC and SAC-CI calculations.

State	Symmetry (C_{2V})	With selection	Without selection
Ground	$^1A_1$	2888	30 810
Excited	$^1A_1$	4529	30 810
	$^1A_2$	4527	30 199
	$^1B_1$	4505	30 381

TABLE II. Orbital energies and characters of the HF orbital.

Symmetry	Character[a]	Orbital energy (a.u.)
	Occupied orbitals	
$5t_2$	$M + O$	− 0.4794
$1e$	$M + O$	− 0.4240
$6t_2$	O	− 0.3306
$1t_1$	O	− 0.2880
$6a_1$	O	− 0.2823
	Unoccupied orbitals	
$7t_2$	$M - O$	0.1857
$2e$	$M - O$	0.2068
$7a_1$	M	0.2173
$8t_2$	O	0.2773

[a] $M \pm O$ denote bonding and antibonding combinations between metal and oxygen. M and O mean localized orbitals on metal and oxygen, respectively.

calculations are small in comparison with those of the CI method of a comparable accuracy.

For assuring the convergence of the results with respect to the size of the active space, we carry out additional SAC/SAC-CI calculations using two smaller active spaces, namely one consisting of the 12 occupied and 19 unoccupied MO's and the other of the 12 occupied and 31 unoccupied MO's. The thresholds used for the selections of the linked and unlinked terms are the same as those used for the larger active-space calculations.

III. RESULTS AND DISCUSSIONS

A. Ground state

The SCF orbital sequence is shown in Table II, which involves only occupied valence and lower unoccupied orbitals up to the $8t_2$ MO. Table II also shows the characters of the SCF orbitals; i.e., M and O denote metal and oxygen atomic orbitals (AO), respectively, and $M \pm O$ mean bonding (+) and antibonding (−) combinations. The lowest two valence orbitals, $5t_2$ and $1e$, are the bonding MO's between the $3d$ orbitals of Mn and the $2p$ orbitals of O, while the unoccupied orbitals, $7t_2$ and $2e$, are the antibonding MO's between them. The occupied $5t_2$ and unoccupied $2e$ MO's have larger amplitudes at the metal AO than in the oxygen AO, though the unoccupied $7t_2$ and occupied $1e$ MO's have reverse relations. The excitations, $5t_2 \rightarrow 7t_2$ and $1e \rightarrow 2e$ work to weaken the covalent Mn–O bonds, while the former excitation slightly increases the ionicity and the latter one reduces it. The $6t_2$ and $1t_1$ MO's are localized on the $2p$ orbitals of the oxygen atoms. The $6a_1$ MO is mainly composed of the $2p$ orbitals of O and partly of the $4s$ orbital of Mn, and it is slightly antibonding between Mn and O.

Table III shows the total energies and the net charges of MnO_4^- calculated by the HF and SAC methods. The Mn–O bond is calculated to be more strongly ionic by the HF method than by the SAC method. The ionic character of the Mn–O bond is relaxed by including electron correlations.

Table IV shows the occupation numbers of the natural orbitals of the SAC wave function. In comparison with the HF ones, the occupations of the $6t_2$ and $1t_1$ MO's decrease more than those of the $5t_2$ and $1e$ MO's. In the unoccupied orbitals, the occupancies of the $7t_2$ and $2e$ MO's increase by including electron correlations. These changes in occupation number result in an increase of the $3d$ occupation of Mn and a decrease of the $2p$ occupation of O. The transition from the $6a_1$ MO seems to reduce slightly the $4s$ occupation of the metal atom.

B. Excited states

Figure 1 shows the electronic spectra of the MnO_4^- ion, the upper one being the experimental spectrum observed by Holt et al.[3] and the lower one the present theoretical spectrum calculated by the SAC-CI method. The values for the vertical excitation energy cited from Ref. 10 are shown in the experimental spectrum. In the T_d symmetry, only the transitions to the $^1T_2$ states are dipole allowed. Table V shows a

TABLE III. Total energies and valence electron populations for the ground state of MnO_4^- calculated by the HF and SAC methods.

| Method | Energy (hartree) | Mn | | | | O | | |
		s	p	d	Charge	s	p	Charge
HF	− 1448.408 13	0.730	0.396	4.479	+ 1.246	1.968	4.599	− 0.562
SAC	− 1448.884 18	0.665	0.418	4.734	+ 1.035	1.962	4.551	− 0.509
Δ[a]	− 0.476 05	− 0.065	+ 0.022	+ 0.255	− 0.211	− 0.006	− 0.045	+ 0.053

[a] The difference between HF and SAC values.

TABLE IV. Occupation number of the HF orbitals and the SAC natural orbitals for the ground state.

Symmetry	HF	SAC	Δ [a]
Occupied orbitals			
$5t_2$	6.0	5.943	− 0.057
$1e$	4.0	3.951	− 0.049
$6t_2$	6.0	5.891	− 0.109
$1t_1$	6.0	5.843	− 0.157
$1a_1$	2.0	1.946	− 0.054
Unoccupied orbitals			
$7t_2$	0.0	0.228	+ 0.228
$2e$	0.0	0.127	+ 0.127
$2a_1$	0.0	0.007	+ 0.007
$8t_2$	0.0	0.018	+ 0.018

[a] The difference between HF and SAC values.

FIG. 1. Experimental and theoretical electronic excitation spectra of MnO_4^-. Experimental spectrum is cited from Ref. 3.

summary of the present SAC-CI results for the singlet excitation energy, oscillator strength, and net charge of the excited state. We assign the observed four bands to the allowed transitions to the $^1T_2$ states. The main configurations of all the excited states shown in Table V are singly excited from either of the $6t_2$, $1t_1$, or $6a_1$ MO to one of the $7t_2$ and $2e$ MO's. The $6t_2$, $1t_1$, and $6a_1$ MO's are mainly made of the oxygen AO, although the $4s$ orbital of Mn partly contributes to the $6a_1$ MO. Both $7t_2$ and $2e$ MO's are delocalized all over the ion and they have antibonding characters between Mn and O. Therefore, the transitions shown in Table V are all roughly characterized as electron-transfer excitations from oxygen to metal.

The lowest excited state is calculated to be the 1^1T_1 state, which has the main configuration of the excitation from $1t_1$ to $2e$, and the calculated excitation energy is 2.18 eV. Since the transition to the 1^1T_1 state is dipole forbidden, the corresponding transition peak is not found in the experimental spectrum of Fig. 1. On the other hand, in the lithium
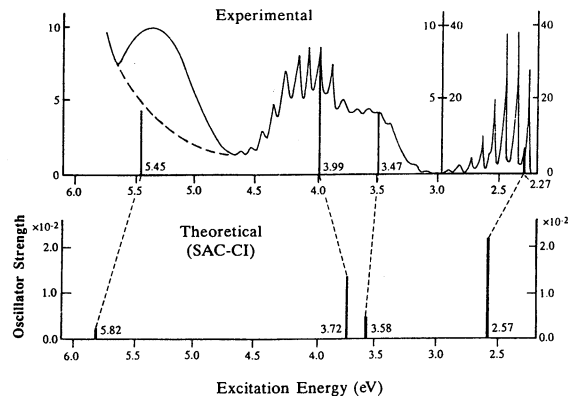
and barium salts, $LiMnO_4 \cdot 3H_2O$ and $Ba(MnO_4)_2 \cdot 3H_2O$, the corresponding transitions are observed at 1.71 and 1.77 eV, respectively.[5] Since the lithium and barium salts belong to the C_{3v} and C_3 symmetries, respectively, these transitions are symmetry allowed.

The first strong band observed at 2.27 eV is assigned to the allowed transition to the 1^1T_2 state, which is characterized as a single excitation from $1t_1$ to $2e$, and the theoretical excitation energy is 2.57 eV. Figure 2 shows a summary of the previous theoretical results. It is seen that our assignment for the first band is the same as those of the ΔSCF (Ref. 13) and SD-CI (Ref. 16) calculations. Hillier et al. showed that the corresponding transition was calculated for the 3^1T_2 (Ref. 10) or 2^1T_2 (Ref. 11) state by the SE-CI method. We show later that the SE-CI method is totally unreliable for this molecule. The excitation energy calculated by the ΔSCF

TABLE V. Summary for the ground and excited states of MnO_4^-.

State	Main configuration	SAC/SAC-CI Excitation energy[a] (eV)	Oscillator strength	Net charge Mn	Net charge O	Experimental Excitation energy (eV)	Experimental Oscillator strength
XA_1	HF	0.00		+ 1.035	− 0.509		
$1T_1$	$1t_1 \rightarrow 2e$	2.18	Forbidden	+ 0.670	− 0.417	(1.71 − 1.77)	
$1T_2$	$1t_1 \rightarrow 2e$	2.57 (+ 0.30)	0.0202	+ 0.683	− 0.421	2.27	Strong
$2T_1$	$6t_2 \rightarrow 2e$	3.33	Forbidden	+ 0.761	− 0.440		
$1E$	$1t_1 \rightarrow 7t_2$	3.41	Forbidden	+ 0.880	− 0.470		
$2E$	$6a_1 \rightarrow 2e$	3.54	Forbidden	+ 0.775	− 0.444		
$2T_2$	$1t_1 \rightarrow 7t_2$	3.58 (+ 0.11)	0.0045	+ 0.884	− 0.471	3.47	Weak
$3T_2$	$6t_2 \rightarrow 2e$	3.72 (− 0.27)	0.0136	+ 0.771	− 0.443	3.99	Strong
$3T_1$	$1t_1 \rightarrow 7t_2$	4.12	Forbidden	+ 0.857	− 0.464		
$1A_2$	$1t_1 \rightarrow 7t_2$	4.46	Forbidden	+ 0.832	− 0.458		
$4T_1$	$6t_2 \rightarrow 7t_2$	5.30	Forbidden	+ 0.923	− 0.481		
$2A_1$	$6t_2 \rightarrow 7t_2$	5.41	Forbidden	+ 0.920	− 0.480		
$3E$	$6t_2 \rightarrow 7t_2$	5.47	Forbidden	+ 0.873	− 0.468		
$4T_2$	$\left(\begin{array}{c} 6t_2 \rightarrow 7t_2 \\ 6a_1 \rightarrow 7t_2 \end{array} \right.$	5.82(+ 0.37)	0.0022	+ 0.877	− 0.469	5.45	Strong

[a] Values in parentheses show the difference from the experimental values.
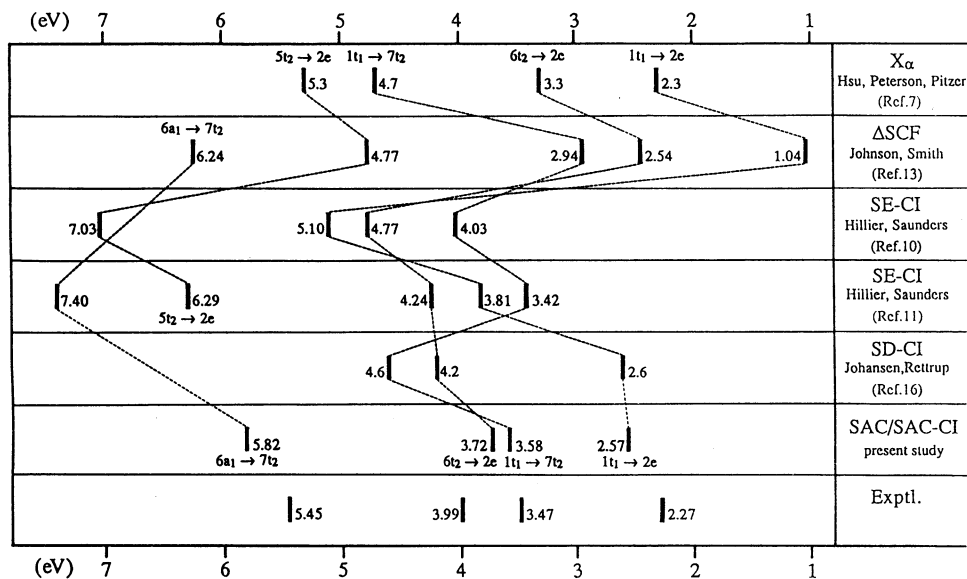
FIG. 2. Summary of the previous and present theoretical results for the dipole-allowed electronic excitations to the $^1T_2$ states of MnO_4^-.

procedure is 1.04 eV, which is about 1.2 eV smaller than the experimental value. The correlation error in the ground state is much larger than that in the excited state.

Figure 3 shows the SE-CI and SAC/SAC-CI results obtained from the present calculations. We use several different sizes of active spaces for the SAC/SAC-CI calculations. The calculations for the [12×41] active space is the most reliable one. The SE-CI calculation gives the $1t_1 \rightarrow 7t_2$ state as lowest and the $1t_1 \rightarrow 2e$ state as the third allowed state at 4.75 eV above the ground state. This result is similar to the one due to Hillier et al.[10,11] On the other hand, by the SAC/SAC-CI method, the lowest transition is always to the $1t_1 \rightarrow 2e$ state. As the size of the active unoccupied space increases, the excitation energy decreases and comes closer to the experimental value. The best value is 2.57 eV, which is still larger than the experimental value by 0.3 eV. We there-

fore conclude that for a reasonable description of the first dipole allowed transition, it is important to include large enough electron correlations with a large active space. This is necessary for a sufficient relaxation of the valence electrons.

Table V shows the excitation energies, main configurations, oscillator strengths, and net charges for the ground and excited states presently calculated by the SAC/SAC-CI method. They involve both dipole-allowed and forbidden states. For the lowest two states (1^1T_1 and 1^1T_2 states), the transitions are from the $1t_1$ MO to the $2e$ MO, so that electron is transferred from oxygen to mainly the $3d$ orbital of Mn. Therefore, the polarity of the Mn–O bond is much reduced by this transition.

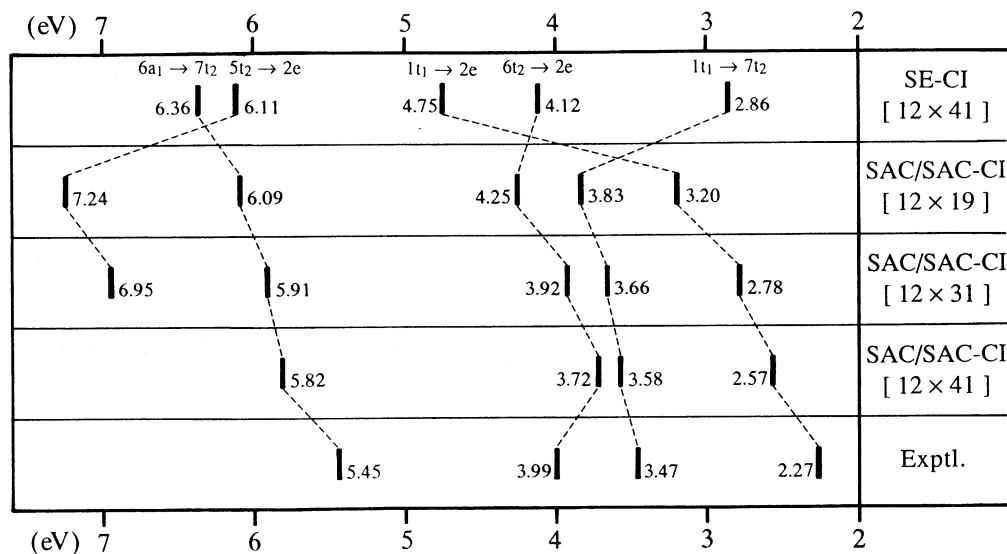The second and third dipole allowed states, 2^1T_2 and 3^1T_2 states have the main configurations expressed as

FIG. 3. Dipole-allowed transitions ($^1T_2$ states) of MnO_4^- calculated by the SE-CI and SAC/SAC-CI methods using different active spaces.

$1t_1 \rightarrow 7t_2$ and $6t_2 \rightarrow 2e$, respectively. The weak band observed at 3.47 eV is assigned to the transition to the 2^1T_2 state and the strong band at 3.99 eV to the transition to the 3^1T_2 state. The calculated excitation energies at 3.58 and 3.72 eV, respectively. The calculated oscillator strength is smaller for the former than for the latter. This order agrees with the order of the strengths of the experimental peaks.

The present assignments for these two transitions are different from those of the previous studies. The assignments due to the $X\alpha$ (Ref. 7) and ΔSCF (Ref. 13) calculations are reverse to ours. In the SD-CI study,[16] the second experimental band is assigned to the forbidden transitions to 1^1E and 2^1T_1 states, which are characterized by the excitations from $6a_1$ to $2e$ and from $6t_2$ to $2e$, respectively. Furthermore, Johansen et al. assigned the third and fourth bands to the transitions to 2^1T_2 ($6t_2 \rightarrow 2e$) and 3^1T_2 ($1t_1 \rightarrow 7t_2$) states, respectively. However, their main configurations correspond to those of the 3^1T_2 and 2^1T_2 states of the present results, respectively.

The fourth band observed at 5.45 eV is assigned by the present calculation to the transition to the 4^1T_2 state calculated at 5.82 eV above the ground state. The discrepancy from the experimental value is 0.37 eV. The main configurations are the mixtures of $6a_1 \rightarrow 7t_2$ and $6t_2 \rightarrow 7t_2$. The calculated oscillator strength is 2.2×10^{-3}, relatively small, though the intensity of the observed band is strong.

The present assignment for the fourth band is different from those of the previous studies. As shown in Fig. 2, the ΔSCF (Ref. 13) and SE-CI (Refs. 10 and 11) calculations assigned this peak to the excitation, $5t_2 \rightarrow 2e$, and the fifth $^1T_2$ state to $6a_1 \rightarrow 7t_2$. The same results are obtained by the present SE-CI calculations. As shown in Fig. 3, the SE-CI excitation energy to the $5t_2 \rightarrow 7t_2$ state (4^1T_2) is smaller than those of the corresponding state (5^1T_2) by the SAC/SAC-CI method. On the contrary, the excitation energies to the $6a_1 \rightarrow 7t_2$ state shows reverse relationship. Thus, the magnitude of the correlation energy is different from one excited state to another.

IV. CONCLUDING REMARKS

We have applied the SAC/SAC-CI method to the calculations of the ground and excited states of MnO₄⁻. With the use of the three different active spaces, we have examined the convergence of the results of the SAC/SAC-CI calculations.

For the ground state, the five MO's, three $5t_2$ MO's, and two $1e$ MO's describe the valence electrons. They compose the four Mn–O bonds and the one lone pair. Electron correlations work to relax charge polarizations of the Mn–O bonds.

The theoretical excitation spectrum calculated by the SAC-CI method reproduces well the experimental spectrum. The observed four peaks are assigned as being due to the dipole-allowed transitions to the $^1T_2$ state. The maximum discrepancy between the experimental and theoretical excitation energies is 0.37 eV. This SAC–CI assignment differs from the previous ones as summarized in Fig. 2. These electronic transitions below 6 eV are characterized as the transitions from the nonbonding orbitals of oxygens to the antibonding orbitals between metal and oxygens. There-

fore, along with the transitions, electrons flow from the oxygens to the metal, reducing the polarity of the Mn–O bonds.

The present study shows that electron correlations are quite important even for a qualitative assignment of the excitation spectrum of MnO₄⁻. The SE-CI results are totally unreliable as shown in Fig. 3. Most of the previous theoretical results are also unreliable, since they do not include sufficient amount of electron correlations. We propose the present SAC-CI assignment as a reliable one, including a sufficient amount of electron correlations. The SAC-CI method seems to be useful for studying excited states of metal complexes, as have already been shown also for several other complexes.

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