Excited electronic states of MnO$_4^-$: Challenges for wavefunction and density functional response theories

Nuno M.S. Almeida, Russell G. McKinlay, Martin J. Paterson *

Institute of Chemical Sciences, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, Scotland

A B S T R A C T

The lowest excited electronic states of the permanganate ion MnO$_4^-$ are calculated using a hierarchy of coupled cluster response approaches, as well as time-dependent density functional theory. It is shown that while full linear response coupled cluster with singles and doubles (or higher) performs well, that permanganate represents a stern test for approximate coupled cluster response models, and that problems can be traced to very large orbital relaxation effects. TD-DFT is reasonably robust although errors around 0.6 eV are still observed. In order to further investigate the strong correlations prevalent in the electronic ground state large-scale RASSCF calculations were also performed. Again very large orbital relaxation in the correlated wavefunction is observed. Although the system can qualitatively be described by a single configuration, multi-reference diagnostic values show that care must be taken in this and similar metal complexes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The theoretical study of the excited states of transition metal complexes has, over previous years, presented a particular challenge to researchers due to the complex nature of the electronic spectra of many transition metal compounds. A high density of states, of often different chemical character in a narrow energy range, gives rise to broad–featureless experimental spectra [1,2]. We have previously shown how the supposedly simple TiO$_2$ molecule is challenging to describe [3]. The challenges when trying to accurately study the electronic excited states of transition metal complexes present a hurdle on the path to fully understanding the rich and varied reactive photochemistry that many transition metal complexes display, with more cases being reported regularly, see for example [4–11]. There are also a number of well-known complexes that despite their modest size and simple structure have been classed as 'tough' examples when trying to fully understand the nature of their ground and electronic excited states due to often poor agreement between many theoretical methods and experiment [12]. It is not always clear when such difficulties will be encountered. One such case that is the subject of this study is the permanganate ion, MnO$_4^-$ [13–20]. This d^0 complex is a very well investigated molecule in chemical research, across many different areas, going back as far as the 1930s [21,22]. A number of

studies have been published concerning a theoretical treatment of its ground and excited electronic states. A large range of theoretical studies exist in the literature including older studies based in Hartree–Fock [23], post Hartree–Fock [24], and older density functional theory (DFT) methods, [25] and a time-dependent-DFT (TD-DFT) treatment has also been performed [14,26–29]. A study including a combination of coupled cluster theories and perturbation theory, including EOM-CCSD, has also been reported by Nooijen [30].

One of the most recent and comprehensive studies of this system was reported by Jose et al. [31] in which they use a DFT approach in which they analyse the excitation energies and oscillator strengths of the lowest excited bright states and also optimise the structures of these states and study their vibrational modes, generating vibronically resolved spectra via the Frank–Condon approximation. It was found that the optimised structures of the first three excited states were distorted from the tetrahedral ground state structure with the first excited state having C$_{3v}$ symmetry, the second C$_{2v}$ and the third D$_{2d}$ symmetry. The authors believed these states were fluxional with distortions occurring via Jahn–Teller distortions. Indeed Jahn–Teller distortions could be expected for this highly symmetric system as the nature of the excitations involves transitions amongst orbitally degenerate frontier orbitals. The natures of the transitions that make up the second and third experimental bands were found to mix strongly with each other. This feature is rather common to the electronic excited states of many transition metal complexes and it is the

ability of their excited states to mix in different ways that allows some of the most varied and rich photochemistry to take place, see for example [32–35].

The hierarchy of coupled cluster response methods [36–41] are a group of methods for studying electronic excited states that have a number of beneficial features such as the ability to treat excited states of different chemical character on a equal footing, where unlike methods such as complete active space self-consistent field (CASSCF), and CAS with a second-order perturbation treatment of dynamical correlation (e.g., CASPT2) an active space of orbitals does not need to be specified *a priori*. So far these methods have found much success when applied to organic systems, see for example [42,43], but the performance of the lower cost CC2 method, and to some extent the higher cost CC3 method has been found to be poor when applied to some transition metal systems [3,44].

Given the current ambiguities surrounding the state ordering and nature of the initial excited electronic states of MnO_4^-, and its importance as a paradigm metal oxide complex, we aim to apply the hierarchy of coupled cluster response methods along with large scale CASSCF, and the related restricted active space self-consistent field (RASSCF) method, and TD-DFT using modern Coulomb attenuated functionals (here CAM-B3LYP [45,46]) to this system, most of these for the first time. Secondly we wish to use CASSCF and RASSCF to determine the nature of the electronic structure of the ground electronic state of MnO_4^-, and detail the balance of static and dynamic correlation present, and to understand orbital relaxation in the ground state. The purpose of applying CC2 and CC3 response methods to understand the performance of these popular correlated excited state treatments to a paradigm molecule such as MnO_4^-, where some of the previous preliminary results indicate that transition metal oxides molecules and clusters present significant challenges. We also hope that this detailed set of results for the lowest excitations in MnO_4^- will help to resolve some of the current ambiguities regarding the ordering of the initial excited states of this system. Finally we also look to compare these methods with modern Coulomb attenuated density functionals (CAM-B3LYP) that have been developed to describe charge transfer excitations within TD-DFT, which should be paramount in describing the LMCT states in a d^0 oxide complex.

2. Computational details

MnO_4^- was optimised in its ground electronic state ($^1A_1$) with tetrahedral (T_d) symmetry using a variety of double and triple zeta quality all electron basis sets in conjunction with Hartree–Fock, coupled cluster singles and doubles (CCSD), and Bruckner doubles (BD) wavefunction methods, together with a variety of density functionals. All optimised structures were confirmed as minima via frequency calculations (analytical if available, otherwise numerical).

The optimised structure at the B3LYP/aug-cc-pVTZ level was then used to perform calculations of the lowest electronic singlet excited states with the coupled cluster linear response (LR) coupled cluster hierarchy CCS, CC2, CCSD and CC3, along with perturbative corrected methods CIS(D) and CCSDR(3). The correlated response methods were performed with an all-electron atomic natural orbital (ANO) basis set contracted to 6s5p4d3f1g on manganese, [47] together with the cc-pVTZ basis set on the oxygen atoms. The all-electron correlated calculations invoked a 13 orbital frozen core (O 1s, Mn 1s2s2p3s3p). Trial calculations correlating these orbitals only had a minor effect on excitation energies. For comparison the EOM-CCSD method with the cc-pVTZ basis on all atoms was tested to compare with LR-CCSD. These formally give exactly the same excitation energies, although the transition

moments are more accurate for LR-CCSD. Abelian symmetry (D_2) was used in all correlated excited state calculations.

A wide variety of CC methods have been developed over the years in order to retain the overall accuracy of the cluster expansion while reducing the computational scaling. Most of these ideas are inspired by many-body perturbation theory in which terms in the cluster equations are evaluated or discarded depending on the order in which they contribute to the correlation energy. For electronic ground states the most well known approximation is the CCSD(T) approach in which CCSD equations are solved and the resulting singles and doubles amplitudes are used in the triples equations from perturbation theory. This reduces the N^8 scaling of full CCSDT to N^7, allowing triples correlated calculations to be routinely performed for the ground states of small to medium sized molecules. There exist a similarly rich variety of CC approximations for electronically excited states as obtained from response function theory [30,36,37,39–41]. However, a simple correlation contribution analysis is complicated by virtue of the fact that in the absence of the external perturbation of response theory the singles contribute to the correlation energy (via Brillouin's Theorem) at second order and above, but contribute at zeroth order when the external perturbation is present. Thus, for a balanced description of singles the CCn methods have been developed in which singles amplitudes are used to similarity transform all operators, and then this modified order counting (keeping only the lowest non-vanishing order) is performed on the doubles equation of CCSD to give CC2 [40,41], triples equation of CCSDT to give CC3 [39], etc. These have scalings of N^5 and N^7 respectively, and together with the full CC methods generate a systematic hierarchy of CCS, CC2, CCSD, CC3, CCSDT,..., with each one giving response functions correct to the next order in the fluctuation potential [41]. For ground electronic states one can think of CC2 and CC3 as similar to MP2 and CCSD(T) respectively, but with the addition of orbital relaxation. For excited states calculated via response functions the CCn methods provide a balanced systematic series applicable to a wide range of molecules. Indeed, for organic systems this hierarchy has proved exceptionally valuable in benchmarking a plethora of excited state approaches [42,43]. However, for certain inorganic molecules we have shown that the same levels of accuracy may not be obtained and the nature of the electron correlation in the ground (reference) state the Refs. [3,4].

Within time-dependent density functional theory (TD-DFT) the excited states were calculated using the B3LYP and the CAM-B3LYP functionals, also with the cc-pVTZ basis. CAM-B3LYP was designed to more correctly describe charge transfer (CT) states by varying the amount of exact Hartree–Fock exchange with inter-electronic distance to give a better long range potential, known to be important for CT states [45,46].

In order to examine the nature of the electronic ground state in more detail restricted active space self-consistent field (RASSCF) calculations were performed using an overall active space comprising of 40 electrons and 39 orbitals partitioned into a 17 orbital RAS1, 9 orbital RAS2, and 13 orbital RAS3. The RAS1 space consists of those orbitals strongly occupied outside the doubly occupied set and we find that 17 orbitals are required here. The orbital occupancies (diagonal elements of the one electron density matrix) for the RASSCF orbitals are given in Table S1 in supporting information. The RAS2 space includes those orbitals that are partially occupied, the degree of partial occupancy indicating how much multi-configurational character there is in the wavefunction. Finally the RAS3 space contains weakly occupied orbitals. All excitations are allowed in RAS2, while single particle and holes and allowed in RAS3 and RAS1 respectively. This generates 2,984,730 singlet configurations using Slater determinants as the many electron basis functions. Although the orbitals in the respective restricted space partitions are invariant to separate unitary transformations it is