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Calculations of the low-lying excited states of the TiO$_2$ molecule

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We present calculations of the lowest excited electronic states of the TiO$_2$ molecule. These are computed using several correlated wavefunction response based methods, as well as time-dependent density functional response theory using a range of functionals. Surprisingly lower cost wavefunction based methods, in particular the second-order CC2 and CIS(D) methods, completely fail to describe the lowest $^1B_2$ and $^1A_2$ states of the molecule. Density functional methods fare better but still show considerable variation amongst functionals. Thus TiO$_2$ provides a strenuous test for correlated excited state methods. © *2010 American Institute of Physics*. [doi:10.1063/1.3515477]

I. INTRODUCTION

The structure and bonding in TiO$_2$ clusters has been the subject of intense study due to the enormous technological potential for TiO$_2$ materials in a diverse range of fields.[1,2] Furthermore, TiO$_2$ is often seen as the simplest transition metal oxide due to its relatively simple ground state electronic structure.[1,3–5] For these reasons experimental and theoretical studies on (TiO$_2$)$_n$ nanoclusters have been ongoing to understand the basic nature of the bonding, electronic transitions, electron attachment, quantum size effects, and how the electronic structure of the clusters evolves to that of the bulk materials (e.g., the rutile and anatase phases).[3–12] Indeed highly correlated methods such as CCSD(T) have been used on neutral and anion clusters up to $n = 4$ and these provide the most accurate benchmark results available for ground state structures.[8] As a part of this the isolated TiO$_2$ molecule has been the subject of several studies aimed at elucidating its geometry and electronic spectroscopy.[3–12] Below we present the first applications of correlated response theory to the problem of the excited states of this molecule.

The development of computational methods to treat electronically excited states has gathered pace in the last decade or so. In addition to complex multireference techniques applied to small and medium sized molecules (e.g., MRCI and CASPT2), nowadays a correlated treatment of electronic excitations is possible via the coupled cluster response hierarchy (CCS, CC2, CCSD, and CC3). Here a systematic improvement in molecular properties (e.g., excitation energies and transition moments) is obtained at each subsequent level of the hierarchy.[13,14] The calculation of excitation energies in larger molecular systems is possible using both wavefunction and density functional techniques. For example the second-order CC2 response method has emerged as a reliable and relatively low cost way to study a range of states in a balanced manner. Hättig has presented a review of second-order excited state methods,[15] while Sauer *et al.* have analyzed the performance of such methods in organic molecules.[16]

The CC2 method in particular has become invaluable to account for multiconfigurational character in excited states (e.g., state-mixing), and in the study of charge transfer excitations. Time-dependent linear response density functional theory (TD-DFT) also now has a prominent position in the study of excited states of large molecular systems.

As a part of our on-going studies on TiO$_2$ nanoclusters using correlated electronic structure methods,[17] we have studied the TiO$_2$ molecule in some detail. In particular we have investigated the electronic transitions to the lowest singlet and triplet excited states as detailed below using an array of correlated methods and one-particle basis sets. We also compare with time-dependent density functional response theory. We show that some second order response methods have severe problems in describing the lowest excitations in this system.

II. RESULTS AND DISCUSSION

The geometry of TiO$_2$ was optimized using B3LYP in conjunction with the cc-pVTZ basis (*vide infra*). The ground electronic state is a closed-shell singlet with a C$_{2v}$ geometry. The optimized geometrical parameters are TiO bond-length: 1.644 Å and OTiO bond-angle: 111.9°. These compare well with the detailed MRCI study by Grein which gave the minimum ground state geometry as TiO bond-length: 1.640 Å and OTiO bond-angle: 112.0°.[7] Other theoretical work at the CCSD(T)/aug-cc-pVTZ level gave optimized geometrical parameters of TiO bond-length: 1.663 Å, and OTiO bond-angle: 112.4°.[8]

The one electron basis sets used for the coupled-cluster calculations discussed in detail below were atomic natural orbitals (ANOs). For oxygen the ANO-1 set[18] was contracted (6s5p3d2f)/[4s3p2d1f], while for titanium the ANO-3 set[19] was contracted (8s7p6d5f4g)/[7s6p4d2f1g]. For the density functional linear response calculations the cc-pVTZ basis was used (standard cc-pVTZ for oxygen ([4s3p2d1f] contracted basis functions), and Petersen's cc-pVTZ for titanium[20] ([7s6p4d2f1g] contracted basis functions)).

As the coupled cluster response calculations are benchmark results all electrons were correlated. The effect of tight core correlation functions was determined by comparing

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TABLE I. TiO$_2$ vertical excitation energies (in eV) from 1 $^1A_1$ ground state to lowest singlet and triplet states, obtained with a variety of wavefunction methods using an ANO basis.

	CIS/CCS	CIS(D)	SOPPA	SOPPA(CCSD)	CC2	CCSD	CCR(3)	CC3
1 $^1B_2$	4.433	0.000	−0.914	−1.018	0.219	2.386	2.247	2.370
1 $^1A_2$	5.112	2.285	−0.891	−0.987	0.704	3.045	2.730	2.376
1 $^3B_2$	4.263		−0.873	−0.979	0.284	2.333		2.489
1 $^3A_2$	4.671		−0.844	−0.942	0.748	3.016		2.498
2 $^1B_2$	5.260	0.000	−0.232	−0.368	1.161	3.213	3.053	3.291
1 $^3A_1$	4.267		0.509	0.372	2.764	3.083		3.522
2 $^1A_1$	4.833	0.000	0.624	0.466	2.745	3.315	3.478	3.599
3 $^1A_1$	5.456	0.000	1.059	0.906	3.363	4.027	4.250	3.677
1 $^3B_1$	4.518		0.542	0.414	2.999	3.375		3.804
1 $^1B_1$	4.984	0.000	0.623	0.499	3.061	3.599	3.766	3.890
2 $^1A_2$	5.321	−0.439	1.621	1.462	3.665	3.969	4.175	3.998
2 $^1B_1$	5.230	0.000	0.949	0.833	3.217	3.711	3.889	4.002

linear response CCSD excitation energies for the 1$^1B_2$ and 1$^1A_2$ states using the cc-pwCVTZ basis (Petersen's [9s8p6d3f2g] contraction for titanium,[20] and the standard cc-pCVTZ for oxygen of [6s53d1f] contracted functions). The core correlation functions changed the excitation energy by less than 0.05 eV, while the frozen core approximation (oxygen 1s, titanium 1s2s2p) gave rise to a difference of around 0.1 eV. We note, however, that freezing the titanium semicore (3s3p) gave extremely poor results, out by more than 5 eV for the 1 $^1B_2$ state. The effect of extra diffuse functions was determined by comparing the 1 $^1B_2$ and 1 $^1A_2$ excitation energies using the cc-pVDZ and cc-pVTZ basis sets with their augmented counterparts, aug-cc-pVDZ (standard augmented functions for oxygen giving [4s3p2d], while Petersen's diffuse set[20] was added for titanium to give [7s6p4d2f]), and aug-cc-pVTZ (standard augmented functions for oxygen giving [5s4p3d2f], while Petersen's diffuse set[20] was added for titanium to give [8s7p5d3f2g]). In going from cc-pVDZ to aug-cc-pVDZ both excitation energies increase by around 0.1 eV, while the difference between cc-pVTZ and aug-cc-pVTZ is less than 0.05 eV. We also note that the difference between aug-cc-pVDZ and cc-pVTZ is also less than 0.05 eV. Continuing further in this vein we also checked the effect of adding Rydberg-type orbitals[21] to the basis on the 1 $^1B_2$ state excitation energy. Thus the ANO basis discussed above was augmented with centre-of-mass s, p, d, and f functions with half-integer quantum number ranging from 4.5 to 8.5. At the CCSD level the Rydberg basis gave an excitation energy of 2.381 eV, compared to 2.386 eV without these additional functions. Therefore this state has almost no Rydberg character and is a pure valence excited state.

In Table I we present the results of wavefunction methods including CCS/CIS, which for single-excitation dominated states give excitation energies correct to first-order; a range of second-order methods: CIS(D),[22] CC2,[23] the second-order polarization propagator approximation (SOPPA),[24] SOPPA with CCSD amplitudes replacing MP2 ones (SOPPA-CCSD),[25] and those obtained from the full CCSD linear response function (equivalent to equation-of-motion-CCSD (EOM-CCSD) for excitation energies); and CC3,[26] and CCSDR(3),[27] in which the excitation energies are correct to third-order due to the inclusion of connected triples.

CCSDR(3) is a noniterative approximation to the benchmark CC3 method. The DALTON 2.0 program[28] was used for all wavefunction response based excited state calculations.

In Table II the results of time-dependent linear response Hartree–Fock and density functional theory are presented. For TD–DFT the functionals chosen are the popular B3LYP functional, the Coulomb attenuated extension of this (CAM-B3LYP[29]) designed to correctly describe charge transfer excitations, and the M06L functional[30] from the Truhlar family (expected to give best performance of this family for transition metal containing systems). The GAUSSIAN 09 program[31] was used for these calculations.

It is clear that there is a significant variation with these methods for the electronic states considered: the lowest two singlet states, and the lowest triplet state of each symmetry type. The experimental excitation energy for the S$_1$ state is 2.3 eV, as originally obtained by McIntyre et al.[32] This refers to the adiabatic (0–0) transition, however, so the vertical excitation energy will be a little higher. One of the most recent spectroscopic experiments measured the absorption of TiO$_2$ after preparation of TiO$_2^-$ trapped in a Neon matrix at 6 K, followed by electron detachment of the trapped species.[10] The spectrum thus obtained shows (adiabatic) band onsets around

TABLE II. TiO$_2$ vertical excitation energies (in eV) from 1 $^1A_1$ ground state to lowest singlet and triplet states, obtained with time-dependent (TD) Hartree–Fock and density functional methods using the cc-pVTZ basis.

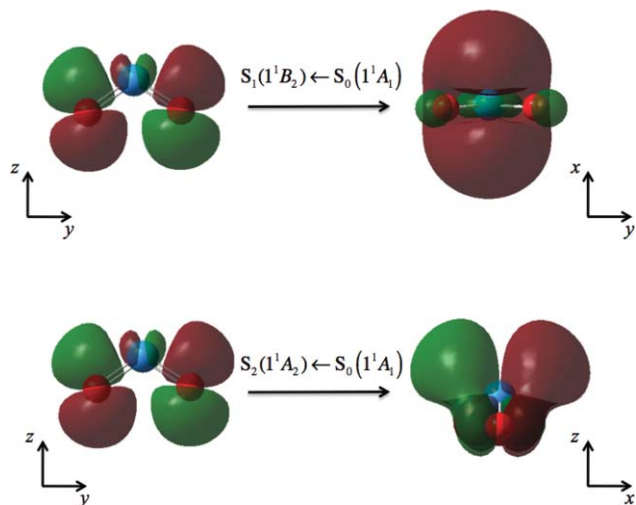|	TD–HF	TD–B3LYP	TD–CAM–B3LYP	TD–M06L
1 $^3B_2$	3.420	2.519	2.744	3.110
1 $^1B_2$	4.397	2.633	2.868	3.172
1 $^3A_2$	3.965	3.119	3.297	3.271
1 $^3A_1$	2.641	3.208	3.254	3.751
1 $^1A_2$	4.906	3.241	3.429	3.367
2 $^1B_2$	4.992	3.353	3.580	3.704
2 $^1A_1$	4.767	3.487	3.696	4.187
1 $^3B_1$	3.969	3.535	3.653	3.989
1 $^1B_1$	4.861	3.788	4.017	4.290
2 $^1B_1$	4.934	4.021	4.143	4.406
2 $^1A_2$	4.946	4.098	4.287	4.716
3 $^1A_1$	5.131	4.209	4.370	4.568

FIG. 1. Natural transition orbitals obtained from TD-CAM-B3LYP/cc-pVTZ for the first two singlet excitations. The S_1 state is represented as a transition from oxygen p_π-orbitals to a titanium $3d_{x^2-y^2}/4s$ orbital, while the S_2 state is represented as a transition from oxygen p_π-orbitals to a titanium $3d_{xz}/4p_x$ orbital.

2.37 and 3.37 eV. These bands were assigned to the $1\,^1B_2$ and $1\,^1B_1$ excited states.

For the $1\,^1B_2$ state CCSD, CCSDR(3), and CC3 are all within 0.1 eV of the experimental value of Ref. 32. Probably either of the third order values is the most accurate, but it should be noted that since vibrational effects (not considered here) can be between 0.01 and 0.1 eV it is difficult to say which is the most accurate value. This state is dominated by single-excitations and is thus appropriate for both coupled-cluster and density functional response theory (all response methods having some problems for doubly-excited states). The CC2 method breaks down completely here with an excitation energy of only 0.21 eV, while the noniterative CIS(D) also breaks down with an excitation energy of almost zero. At the CIS level the first two states of B_2 symmetry are almost 1 eV apart and thus one might not expect any problems related to quasidegeneracy. However, comparing the absolute excitation energies in Table I it is clear that correlation effects are so strong here that such zeroth order states are not appropriate for the perturbative CIS(D) method and also cause serious problems for CC2 and the SOPPA based methods, which generate negative excitation energies. The TD–DFT results for this state are better, especially B3LYP and CAM–B3LYP, although M06L is in error by around 0.6 eV. In Fig. 1 we show the natural transition orbitals[33] for the TD–CAM–B3LYP excitations to the $1\,^1B_2$ and $1\,^1A_2$ states. We note that all methods except TD–HF and CCS/CIS correctly predict that the $1\,^1B_2$ and $1\,^3B_2$ states are very close in energy. Our results for the vertical ground state singlet ($1\,^1A_1$) to the first excited triplet ($1\,^3B_2$) can be compared with previous high-level calculations obtained by explicitly optimizing each state separately.[8] The CCSD(T)/aug-cc-pVDZ adiabatic triplet excitation result of 2.24 eV by Li and Dixon[8] is in line with our CC3 result of 2.489 eV when the excited geometry relaxation is taken into account (*vide infra*). We also note that the ex-

perimental estimate for the HOMO–LUMO band-gap from photoelectron spectroscopy is 2.22 eV.[34] For the $1\,^1B_2$ state the calculated oscillator strengths are: 0.0025 (CC2), 0.0068 (CCSD), 0.0120 (TD–HF), 0.0067 (TD-B3LYP), 0.0060 (TD–CAM–B3LYP), 0.0034 (TD-M06L). The $1\,^1A_2$ state is electric dipole forbidden.

We have also performed complete active space self-consistent field (CASSCF) calculations (using GAUSSIAN 09) with 12 electrons in 12 active orbitals, generating 427350 singlet configurations, in conjunction with the cc-pVTZ basis discussed above. Using state-specific CASSCF there is considerable orbital relaxation in the $1\,^1B_2$ state. The S_1 vertical excitation energy is 2.80 eV. The one-electron density matrix elements for the S_1 state show two singly occupied orbitals, which are almost identical to the TD–CAM–B3LYP natural transition orbitals shown in Fig. 1. The CAS(12,12) T_1 vertical excitation energy is 2.83 eV. Previous calculations indicate that the ground state is quite well described by a single configuration wavefunction.[3,5,8] Our CASSCF results also indicate that this is the case, although it should be noted that the CCSD $\hat{T}_1$ diagnostic is relatively high (0.04). This point has also been noted by Li and Dixon.[8]

The MRCI values of Grein are 2.43 eV for the $1\,^1B_2$ state, 3.09 eV for the $1\,^1A_2$ state, 2.40 eV $1\,^3B_2$ state, and 3.07 eV $1\,^3A_2$ state.[7] For all the states considered, the error in CCSD is on average around 0.3 eV compared to CC3, while for CCS/CIS the error is several electron volts. CC2 fails badly for the $1\,^1B_2$ and $1\,^{1,3}A_2$ states but performs better for the states above these. CIS(D) fails for all states with the strange exception of the $1\,^1A_2$ state in which CIS(D) is fortuitously within 0.09 eV of the CC3 result. We also note that CC3 gives much closer excitation energies for the $1\,^1B_2$ and $1\,^1A_2$, and $1\,^3B_2$ and $1\,^3A_2$ pairs of states. This is not seen in CCSD or CCSDR(3) where the $^1A_2$ dark state excitation energy is over 0.5 eV above that of the $1\,^1B_2$ state.

Although the main focus of this paper is to compare vertical excitation energies using a variety of computational methods we have also investigated the adiabatic excitation energy of the lowest excited S_1 ($1\,^1B_2$) state, as detailed in Table III. The excited state geometry was optimized at the equation-of-motion CCSD (EOM–CCSD) level (using

TABLE III. Comparison of TiO2 $1\,^1B_2 \leftarrow 1\,^1A_1$ vertical and adiabatic excitation energies (in eV).

Method[a]	Vertical[b]	Adiabatic[c]
CIS/CCS	4.433	4.082
CIS(D)	0.000	−1.239
CC2	0.219	−0.573
CCSD	2.386	2.062
CCR(3)	2.247	1.864
CC3	2.370	2.083
TD-B3LYP	2.633	2.345
TD-CAM-B3LYP	2.868	2.593
TD-M06L	3.172	2.883

[a]ANO basis for CC response (all electrons correlated), and cc-pVTZ basis for TD–DFT.
[b]Calculated at ground state B3LYP/cc-pVTZ optimized geometry.
[c]Calculated at $1\,^1B_2$ state EOM–CCSD/cc-pVTZ optimized geometry.

TABLE IV. Comparison of permanent electric dipole moments of 1 $^1A_1$ and 1 $^1B_2$ states.

Method[a]	1 $^1A_1$ [b]	1 $^1B_2$ [c]
CCS	8.07 D	4.12 D
CC2	3.60 D	…
CCSD	6.74 D	3.70 D
CCSD(T)	7.00 D	…
MRCI[d]	6.73 D	5.07 D
Expt.[e]	6.33 ± 0.07 D	2.55 ± 0.08 D

[a] ANO basis (all electrons correlated).
[b] Coupled cluster results, from orbital unrelaxed response, calculated at ground state B3LYP/cc-pVTZ optimized geometry.
[c] Coupled cluster results, from orbital unrelaxed response, calculated at 1 $^1B_2$ state EOM-CCSD/cc-pVTZ optimized geometry.
[d] Reference 7.
[e] Reference 11.

GAUSSIAN 09), using the cc-pVTZ basis discussed above. The geometry for this state is not linear, as predicted by earlier studies,[3] but rather has a OTiO angle of 101.0°, while the TiO bond-length is 1.672 Å. TD–DFT geometry optimization for this state gives very similar results: OTiO angle of 100.4° and TiO bond-length of 1.672 Å for TD–B3LYP, and OTiO angle of 104.8° and TiO bond-length of 1.659 Å for TD–CAM–B3LYP. This is in good agreement with the most recent spectroscopic characterization of TiO_2 which shows vibrational progressions associated with the $^1B_2$ transition consistent with the OTiO angle reducing, and the TiO bonds lengthening while maintaining C_{2v} symmetry.[10–12] The adiabatic excitation energies in Table III are around 0.3–0.4 eV lower than the corresponding vertical excitation energy, and the poor performance of CIS(D) and CC2 is again apparent.

Finally, the most recent spectroscopic characterization of the molecule used Stark effect spectroscopy to determine the permanent electric dipole moments of the ground 1 $^1A_1$ state and 1 $^1B_2$ excited state.[11,12] We have also computed these properties at the optimized geometries for each state (Table IV). For the ground state the CCSD and CCSD(T) methods perform well, although CCSD(T) is slightly further from the experimental value than CCSD or the MRCI results in Ref. 7. It has been found that due to the charge transfer in the 1 $^1B_2$ excited state, from O to Ti (Fig. 1), that the dipole moment of this state is greatly reduced (to around 2.55 D). Our CCSD result for this state is in reasonable agreement with Ref. 11 at 3.70 D. The only other theoretical estimate of this property came from the MRCI studies in Ref. 7, which gave a value of 5.07 D. Clearly this is a challenging electronic state and future computation of the geometry and dipole moment (also including vibrational averaging) at third-order or higher in a large basis set is desirable to fully reconcile with experiment.

III. CONCLUSIONS

On the basis of these results we conclude that caution should be exercised when applying lower cost excited state response methods to some transition metal oxide systems, even though *a priori* it would be expected that there should

be few problems regarding the nature of the system and the states involved. Strong but differing electron correlation effects present in the ground and valence excited electronic states may present problems in such systems. These effects are not so strong as to invalidate single-reference approaches completely, and CCSD works very well, and DFT can also do so. However, the approximate second-order approaches discussed above may breakdown when applied to such systems.

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