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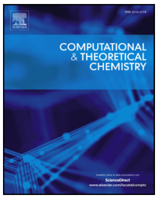

The low-lying triplet electronic excited states of TiO_2 and ZrO_2: A symmetry adapted cluster–configuration interaction (SAC-CI) study

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ABSTRACT

The vertical excitation energies and electron detachment energies to the low-lying triplet excited states of TiO_2 and ZrO_2 were calculated at the SAC-CI/aug-cc-pVTZ levels. The vertical electron detachment energies to the triplet excited states of TiO_2 were compared with previous photoelectron spectra. Possible candidate states for the unassigned bands in the previous photoelectron spectrum were found. Several triplet excited states of TiO_2 and ZrO_2 were optimized at the SAC-CI/aug-cc-pVDZ and SAC-CI/def2-SVPD levels, respectively. The adiabatic excitation energies and electron detachment energies to the selected triplet states were obtained by single-point calculations at the SAC-CI/def2-TZVPPD level. Density functional theory (BPW91/aug-cc-pVTZ) was also applied to study some of the triplet states for comparison. The calculated electron detachment energies and optimized geometries of the triplet excited states should be useful for studying the photoelectron spectra of TiO_2^- and ZrO_2^-.

1. Introduction

TiO_2 and ZrO_2 belonging to the Group IVB metal oxides are of significant industrial and scientific interest due to their versatile applications. TiO_2 has significant photocatalytic activity in water photolysis [1,2]. ZrO_2 is an important material in the fields of ceramics, catalysts, and gas sensors [3–5]. TiO_2 and ZrO_2 both have wide band gaps and can work as *n*-type semiconductors [6]. Studies of MO_2 (M = Ti and Zr) monomers and their clusters $(MO_2)_n$ are meaningful for understanding the chemistry of the MO_2-based materials. Molecular clusters provide connections between a single molecule and solid state materials and have been considered as simplified models for investigating the behavior of bulk materials. Investigations of the MO_2 monomers can help in understanding the chemistry of $(MO_2)_n$ clusters. In addition, the TiO_2 molecule which was observed at radio wavelengths around the red supergiant VY CMa [7] is an interstellar molecule and is of interstellar interest.

The MO_2 molecule and their clusters $(MO_2)_n$ have been extensively studied, both experimentally [8–21] and theoretically [22–37]. The rotational spectrum of TiO_2 was recorded using Fourier transform microwave spectroscopy, and the effective bond length of 1.651 Å and bond angle of 111.57° were obtained [11]. The excitation energy and vibrational frequencies of the A^1B_2 state of TiO_2 were determined from the electronic spectrum [13,14]. The photoelectron spectra of TiO_2^- anion and its cluster anions $(TiO_2)_n^-$ were recorded [15–17], and the electron affinities of the neutral clusters were determined. The investigation of the photoelectron spectra showed that the band gaps of $(TiO_2)_n$ clusters increased with the size of the clusters and approached the bulk limit when n = 7–10 [16]. The X and A bands in the photoelectron spectra were assigned to the Ti(3d)-derived and O(2p)-derived bands, respectively.

The bond length and bond angle of ZrO_2 were determined to be 1.7710(7) Å and 108.11(8)°, respectively, by Fourier transform microwave spectroscopy [18]. The excitation energy and vibrational frequencies of the A^1B_2 state of ZrO_2 were obtained from the electronic spectrum [19]. The photoelectron spectra of ZrO_2^- [17,20] and $Zr_2O_4^-$ [21] anions were recorded, and the electron affinities were obtained. The electron affinities of TiO_2 and ZrO_2 were determined to be 1.5892(5) and 1.6397(5) eV, respectively [17]. As far as the author knows, no spectral data concerning the triplet excited states of ZrO_2 or its clusters $(ZrO_2)_n$ were presented in the literature.

The vertical excitation energies of the low-lying singlet and triplet excited states of TiO_2 have been studied using the multi-reference configuration interaction (MRCI) theory [30], time-dependent density functional theory (TD-DFT) [31,32], coupled cluster (CC) theory [31–33], complete active space self-consistent field (CASSCF and CASPT2) [32], and equation-of-motion CCSD (EOM-CCSD) theory [32,34]. The equilibrium geometries and energies of the lowest singlet, triplet, and quintet states in each of the irreducible representations in the C_{2v} point group symmetry were computed at the BPW91/6-

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Table 1
The calculated vertical excitation energies VEEs (eV) and vertical electron detachment energies VDEs (eV) to the low-lying triplet excited states of TiO_2.

States (Types)		VEEs[a]						VDEs[a]		
	Electronic transitions	SAC-CI			Previous calculations			SAC-CI		
		d-S	d-T	A-T	EOM-CCSD[b]	CASPT2[b]	MRCI[c]	d-S	d-T	A-T
X^1A_1 (S_0)								1.573 (1.737)	1.679 (1.826)	1.704 (1.846)
1^3B_2 (A)	$4b_2 \rightarrow 6, 7a_1$	2.456 (2.268)	2.411 (2.196)	2.429 (2.212)	2.324	2.495	2.40	3.933 (3.914)	3.992 (3.915)	4.033 (3.948)
1^3A_2 (B)	$4b_2 \rightarrow 3, 4b_1$	3.066 (2.981)	3.050 (2.795)	3.062 (2.793)	2.996	2.991	3.07	4.428 (4.507)	4.522 (4.400)	4.559 (4.418)
2^3B_2 (C)	$4b_2 \rightarrow 7, 9, 6a_1$	3.206 (3.096)	3.188 (2.948)	3.202 (2.953)	3.114	3.253	3.20	4.569 (4.617)	4.656 (4.552)	4.695 (4.578)
1^3A_1 (A)	$5a_1 \rightarrow 7, 6a_1$	3.210 (3.051)	3.187 (2.957)	3.197 (2.960)	3.072	3.425	3.12	4.610 (4.642)	4.707 (4.622)	4.742 (4.643)
1^3B_1 (A)	$2b_1 \rightarrow 7, 6a_1$	3.476 (3.313)	3.439 (3.225)	3.452 (3.233)	3.332	3.612	3.43	4.785 (4.798)	4.859 (4.785)	4.896 (4.812)
2^3B_1 (B)	$5a_1 \rightarrow 3, 4b_1$	3.562 (3.479)	3.561 (3.322)	3.570 (3.315)	3.474	3.616	3.59	4.899 (4.988)	5.014 (4.916)	5.047 (4.929)
2^3A_1 (B)	$5a_1 \rightarrow 6a_1/2b_1 \rightarrow 3, 4b_1$	3.800 (3.643)	3.784 (3.545)	3.798 (3.550)	3.657	3.886	3.85	5.068 (5.125)	5.186 (5.082)	5.223 (5.101)
2^3A_2 (A)	$1a_2 \rightarrow 7, 6a_1$	3.862 (3.701)	3.809 (3.600)	3.820 (3.607)	3.696	3.932	3.81	5.185 (5.204)	5.245 (5.180)	5.281 (5.205)
3^3A_1 (C)	$2b_1 \rightarrow 3, 4b_1/5a_1 \rightarrow 6a_1$	3.950 (3.869)	3.947 (3.712)	3.957 (3.710)	3.843	4.449	4.00	5.265 (5.290)	5.339 (5.251)	5.376 (5.277)
3^3B_2 (A)	$3b_2 \rightarrow 7, 6a_1$	4.239 (4.056)	4.199 (3.950)	4.204 (3.950)	4.044	4.122	4.02	5.568 (5.559)	5.649 (5.544)	5.678 (5.559)
4^3B_2 (B)	$1a_2 \rightarrow 4, 3b_1$	4.295 (4.222)	4.284 (4.046)	4.291 (4.038)			4.43	5.496 (5.614)	5.597 (5.506)	5.628 (5.520)
3^3B_1 (C)	$2b_1 \rightarrow 6, 7, 9a_1$	4.309 (4.186)	4.292 (4.069)	4.305 (4.071)			4.34	5.550 (5.582)	5.633 (5.553)	5.671 (5.578)
3^3A_2 (B)	$3b_2 \rightarrow 4, 3b_1$	4.398 (4.310)	4.390 (4.155)	4.395 (4.144)				5.651 (5.732)	5.755 (5.665)	5.784 (5.674)
4^3B_1	$4b_2 \rightarrow 2a_2$	4.500 (4.445)	4.508 (4.244)	4.514 (4.231)				5.771 (5.879)	5.895 (5.771)	5.926 (5.777)
4^3A_1 (A)	$4a_1 \rightarrow 7, 6a_1$	4.557 (4.403)	4.512 (4.312)	4.524 (4.319)				5.860 (5.884)	5.930 (5.868)	5.965 (5.892)
4^3A_2 (C)	$1a_2 \rightarrow 6, 7, 9a_1$	4.767 (4.619)	4.715 (4.502)	4.726 (4.507)				6.039 (6.046)	6.084 (6.013)	6.119 (6.039)
5^3B_2 (C)	$3b_2 \rightarrow 6, 9a_1$	4.823 (4.605)	4.755 (4.505)	4.764 (4.512)				6.140 (6.073)	6.164 (6.060)	6.198 (6.087)
5^3A_1 (C)	$4a_1 \rightarrow 6, 9a_1$	5.229 (5.051)	5.195 (4.963)	5.208 (4.970)				6.498 (6.480)	6.564 (6.473)	6.601 (6.500)
5^3B_1 (B)	$4a_1 \rightarrow 3, 4b_1$	5.317 (5.210)	5.278 (5.032)	5.287 (5.026)				6.549 (6.605)	6.618 (6.507)	6.650 (6.521)

[a] The values shown in parentheses were calculated using Space 2.
[b] Ref. [32].
[c] Ref. [30].

311 + G(3*df*) level [30]. The energies relative to the X^1A_1 state were 2.31 and 2.29 eV for the 1^1B_2, and 1^3B_2 states, respectively, at the anion geometry at the MRCI level. These energy values agreed with the experimental term values of 2.4 (2) eV [15] and 2.22 (10) eV (the A band) [16]. The $1^1B_2(S_1)$, $1^1A_2(S_2)$, $1^3B_2(T_1)$, $1^3A_2(T_2)$ states of TiO_2 were optimized at various levels of theory, and the potential energy surfaces of the S_0-S_5 states were investigated at the TD-B3LYP/aug-cc-pVTZ level [32]. Several low-lying singlet excited states of TiO_2 and ZrO_2 were investigated using the symmetry adapted cluster-configuration interaction (SAC-CI) method [35,36]. Some singlet excited states of these two molecules were optimized, and the adiabatic excitation energies were obtained.

The spectrum for the photodetachment process ZrO_2^- (X^2A_1) → ZrO_2 (X^1A_1) + e was simulated by combining high level ab-inito calculations and Franck-Condon factor calculations including allowance of Duschinsky rotation and anharmonicity [37]. The simulated spectrum was in excellent agreement with the experimental spectrum [20]. The $(MO_2)_n$ (n = 1–4) clusters and their anions $(MO_2)_n^-$ were studied using CCSD(T) and DFT methods [31,34]. Possible conformations for the ground electronic states of these clusters and anions were optimized, and their relative energies were obtained. The vertical and adiabatic electron detachment energies to the ground states and first excited states of the $(MO_2)_n$ clusters were computed. These calculated electron detachment energies were compared with the energies of the X and A bands in the experimental spectra [16]. The theoretical results shown in Refs. [31,34] can be used as benchmarks for the computational studies of $(MO_2)_n$ and $(MO_2)_n^-$.

In the photoelectron spectra of $(TiO_2)_n^-$ clusters with n = 1–4 [16], the excited states related to the A bands have been theoretically studied in Ref. [31]. However, the spectral structures with higher binding energies are still unassigned. These unassigned structures could be related to the triplet excited states of the neutral clusters. Knowledge of the triplet excited states of $(MO_2)_n$ is important for studying the photoelectron spectra of $(MO_2)_n^-$ anions. To the best of the author's knowledge, for the triplet excited states of MO_2, only the 1^3A_1 (TiO_2), 1^3A_2 (TiO_2), 1^3B_1 (TiO_2), and 1^3B_2 (MO_2) states have been optimized [30–32,34]. More investigations on the triplet excited states of MO_2 are needed for understanding the photoelectron spectra of MO_2^- anions.

2. Computational details

The vertical excitation energies (VEEs) and vertical electron detachment energies (VDEs) were calculated using the SAC-CI method [38–43] at the experimental geometries [11,17,18] of the ground electronic states of MO_2 and MO_2^-, respectively. The def2-SVPD, def2-TZVPPD [44–46], and aug-cc-pVTZ [44,47,48] (aug-cc-pVTZ-pp for Zr [44,49]) basis sets were applied to calculate the vertical energies (VDEs and VEEs). For simplification, the notions d-S, d-T, and A-X were used to indicate the def2-SVPD, def2-TZVPPD, and aug-cc-pVXZ (aug-cc-pVXZ-pp for Zr) basis sets, respectively. Two active spaces (Spaces 1 and 2) were used to study the triplet states of MO_2. Space 1 included 16 valence electrons for MO_2 [$M(ns^2(n-1)d^2)$] and $O(2s^22p^4)$], where n = 4 for M = Ti and n = 5 for M = Zr. Space 2 included 8 semi-core electrons [$M((n-1)s^2(n-1)p^6)$] and the 16 valence electrons. All the unoccupied molecular orbitals were included in the two active spaces. The singles and doubles linked excitation operators were used in the SAC-CI calculations. Non-variational procedures [40] and direct algorithm [43] were adopted in the calculations. Restricted Hartree-Fock (RHF) orbitals for the X^1A_1 states of MO_2 were used as the reference orbitals. All the calculations were performed using Gaussian 09 program packages [50].

The geometries of the triplet states of MO_2 were optimized under C_{2v} symmetry constraint at the SAC-CI levels. The adiabatic excitation energies (AEEs) and adiabatic electron detachment energies (ADEs) were obtained by single-point calculations at the SAC-CI/d-T level at the SAC-CI-optimized geometries. For simplification, the relative energies described in the context refer to those computed at the SAC-CI/d-T (Space 1) level.

3. Results and discussion

The calculated vertical energies and adiabatic energies (ADEs and AEEs) to the low-lying triplet excited states of TiO_2 are listed in Tables 1 and 2, respectively. The vertical and adiabatic energies to the low-lying