A theoretical search for stable bent and linear structures of low-lying electronic states of titanium dioxide (TiO_2) molecule

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Supplementary Information

Table S1 Calculated equilibrium geometry and vibrational frequencies of the ground state (S_0 $1\,^1A_1$) of TiO_2 with comparison of different basis sets.

Level of theory	Basis set	Equilibrium geometry		Vibrational frequencies			Dipole moment
		r_{TiO} / Å	θ_{OTiO} / °	ν_1 (a_1) / cm^{-1}	ν_2 (a_1) / cm^{-1}	ν_3 (b_2) / cm^{-1}	μ / debye
CASSCF(12,12)	aug-cc-pVTZ	1.654	112.6	1005.8	329.6	945.1	6.92
	MBS-ECP [a]	1.660	114.2	1002.2	316.9	996.3	6.66
CASSCF(16,14)	aug-cc-pVTZ	1.648	113.2	1021.8	326.5	940.0	6.98
	MBS-ECP	1.654	115.2	1017.6	310.6	1005.0	6.68
CASPT2(12,12)	aug-cc-pVTZ	1.672	111.3	924.4	328.0	926.5	6.97
	MBS-ECP	1.682	114.4	–	–	–	6.66
Expt.[b]		1.651	111.6	946.9	330 ± 6	917.1	6.33

[a] The effective core potential developed by the Los Alamos group (ref. S1) and built in the *MOLPRO 2006* program.

[b] Ref. S2, S3 and S4.

Table S2 Calculated properties of the linear structure of the ground state ($1\,^1\Sigma_g^+$) of TiO_2 with comparison of different basis sets.

Level of theory	Basis set	Adiabatic energy [a]	Equilibrium geometry		Vibrational frequencies		
		ΔE_{ad} / eV	r_{TiO} / Å	θ_{OTiO} / °	ν_1 (σ_g^+) / cm^{-1}	ν_2 (π_u) / cm^{-1}	ν_3 (σ_g^-) / cm^{-1}
CASSCF(12,12)	aug-cc-pVTZ	1.507	1.722	180.0	881.6	(340*i*)	719.4
	MBS-ECP [b]	1.286	1.713	180.0	911.1	(332*i*)	859.3
CASSCF(16,14)	aug-cc-pVTZ	1.419	1.713	180.0	–	–	–
	MBS-ECP	1.219	1.705	180.0	–	–	–

[a] With respect to the ground state equilibrium calculated at the same level of theory and basis set; without zero-point energy.

[b] The effective core potential developed by the Los Alamos group (ref. S1) and built in the *MOLPRO* 2006 program.

Table S3 Calculated oscillator strengths upon excitations from the ground state to low-lying singlet excited states of TiO_2.[a]

State	Excitation [b]	TD-B3LYP	TD-HSE06	TD-ωB97X-D	TD-CAM-B3LYP	EOM-CCSD	CASSCF(16,14)	MRCI [b]
$1\,^1B_2$	$6b_2$–$10a_1$	0.0062	0.0070	0.0049	0.0058	0.0077	0.0035	0.014
$1\,^1A_2$	$6b_2$–$4b_1$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$2\,^1B_2$	$6b_2$–$11a_1$	0.0040	0.0045	0.0103	0.0055	0.0080	0.0014	0.010
$2\,^1A_1$	$9a_1$–$10,11a_1$	0.0017	0.0014	0.0000	0.0002	0.0004	0.0029	0.0003
$1\,^1B_1$	$3b_1$–$10,11a_1$	0.0153	0.0195	0.0286	0.0219	0.0209	0.0049	0.041
$2\,^1B_1$	$9a_1$–$4b_1$	0.0001	0.0000	0.0031	0.0003	0.0013	0.0004	0.0007
$2\,^1A_2$	$1a_2$–$10,11a_1$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$3\,^1A_1$	$9a_1$–$11a_1$	0.0040	0.0045	0.0032	0.0036	0.0044	0.0057	0.013
$3\,^1B_2$	$5b_2$–$10,11a_1$	0.0014	0.0057	0.0045	0.0028	0.0013	0.0022	0.008

[a] The excitation energies are shown in **Table 3** in the main text.

[b] Major excitation configurations and MRCI data from ref. S5.

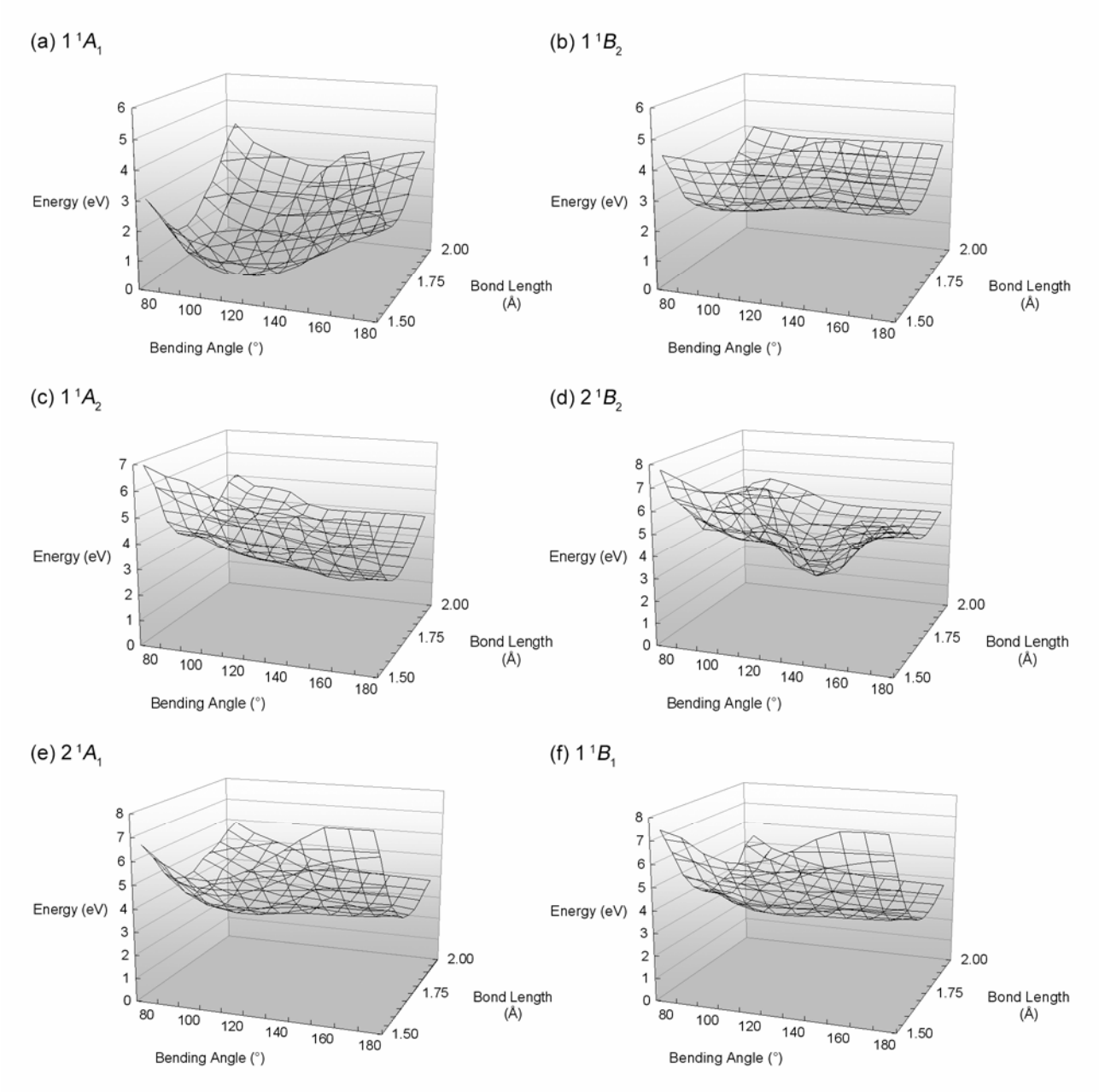

Fig. S1 Two-dimensional multi-reference multi-state CASPT2(12,12)/aug-cc-pVTZ potential energy surface scan of low-lying singlet states of TiO_2.

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