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Ab initio investigation of photoswitches adsorbed onto metal oxide surfaces : the case of donor-acceptor Stenhouse adduct photochromes on TiO2 anatase

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Bond lengths

TABLE 1 – Comparison between the bond lengths of **1a** in the adsorbed and isolated states

Bond type	Adsorbed-phase (Å)	Gas-phase (Å)	Difference (Å)
C 1 – C 5	1.5120	1.5138	0.1741E-02
C 1 – C 6	1.5235	1.5242	0.7765E-03
C 1 – O41	1.4477	1.4472	0.5195E-03
C 1 – O42	1.4647	1.4624	0.2270E-02
C 2 – C 3	1.4504	1.4491	0.1348E-02
C 2 – O39	1.2706	1.2698	0.7724E-03
C 2 – O42	1.3719	1.3768	0.4886E-02
C 3 – C 4	1.4746	1.4731	0.1477E-02
C 3 – C 7	1.4018	1.4045	0.2667E-02
C 4 – O40	1.2490	1.2497	0.7021E-03
C 4 – O41	1.3915	1.3937	0.2236E-02
C 5 – H18	1.0993	1.0996	0.2583E-03
C 5 – H19	1.0993	1.0995	0.1202E-03
C 5 – H20	1.0988	1.0989	0.4583E-04
C 6 – H21	1.1007	1.1005	0.1657E-03
C 6 – H22	1.0996	1.0999	0.3178E-03
C 6 – H23	1.0996	1.0997	0.1276E-03
C 7 – C 8	1.4145	1.4151	0.5331E-03
C 7 – H24	1.0947	1.0947	0.5448E-04
C 8 – C 9	1.4093	1.4046	0.4723E-02
C 8 – O43	1.3594	1.3647	0.5285E-02
C 9 – C10	1.4004	1.4086	0.8223E-02
C 9 – H25	1.0938	1.0939	0.1639E-03
C10 – C11	1.3890	1.3842	0.4733E-02
C10 – H26	1.0921	1.0925	0.4647E-03
C11 – N17	1.3488	1.3596	0.1089E-01
C11 – H27	1.0958	1.0958	0.1626E-04
C12 – C13	1.5283	1.5302	0.1912E-02
C12 – N17	1.4666	1.4664	0.2076E-03
C12 – H28	1.1024	1.1023	0.1688E-03
C12 – H29	1.1005	1.1020	0.1560E-02
C13 – H30	1.1015	1.1016	0.8073E-04
C13 – H31	1.1004	1.1011	0.7082E-03
C13 – H32	1.1004	1.1004	0.2464E-05
C14 – C15	1.5377	1.5493	0.1165E-01
C14 – N17	1.4588	1.4563	0.2478E-02
C14 – H33	1.1025	1.1032	0.7319E-03
C14 – H34	1.1003	1.1009	0.5797E-03
C15 – C16	1.5054	1.5057	0.3774E-03
C15 – H35	1.1000	1.0995	0.4331E-03
C15 – H36	1.1000	1.1000	0.2340E-04
C16 – O44	1.2973	1.3787	0.8144E-01
C16 – O45	1.2964	1.2466	0.4980E-01
H37 – O43	1.0478	1.0414	0.6425E-02

TABLE 2 – Comparison between the bond lengths of **2a** in the adsorbed and isolated states

Bond type	Adsorbed-phase (Å)	Gas-phase (Å)	Difference (Å)
C 1 – C 2	1.5141	1.5155	0.1364E-02
C 1 – H18	1.0991	1.0991	0.6112E-04
C 1 – H19	1.0996	1.0999	0.2572E-03
C 1 – H20	1.0995	1.0998	0.2453E-03
C 2 – C 3	1.5256	1.5278	0.2146E-02
C 2 – O39	1.4601	1.4579	0.2146E-02
C 2 – O40	1.4613	1.4605	0.8031E-03
C 3 – H21	1.1001	1.1005	0.4037E-03
C 3 – H22	1.1000	1.1006	0.5439E-03
C 3 – H23	1.1002	1.0994	0.8180E-03
C 4 – C 5	1.4242	1.4155	0.8730E-02
C 4 – O40	1.3937	1.3998	0.6146E-02
C 4 – O42	1.2702	1.2750	0.4887E-02
C 5 – C 6	1.4253	1.4180	0.7270E-02
C 5 – C 7	1.4873	1.4895	0.2190E-02
C 6 – O39	1.3941	1.4007	0.6591E-02
C 6 – O41	1.2677	1.2705	0.2861E-02
C 7 – C 8	1.5492	1.5437	0.5474E-02
C 7 – C11	1.5405	1.5411	0.6121E-03
C 7 – H24	1.1067	1.1070	0.3728E-03
C 8 – C 9	1.4806	1.4825	0.1852E-02
C 8 – O43	1.2480	1.2491	0.1147E-02
C 9 – C10	1.3484	1.3493	0.8771E-03
C 9 – H25	1.0900	1.0903	0.3121E-03
C10 – C11	1.5027	1.5019	0.7801E-03
C10 – H26	1.0941	1.0947	0.5965E-03
C11 – N17	1.5247	1.5284	0.3783E-02
C11 – H36	1.1039	1.1048	0.9165E-03
C12 – C13	1.5185	1.5175	0.1019E-02
C12 – N17	1.5218	1.5231	0.1325E-02
C12 – H27	1.1044	1.1072	0.2718E-02
C12 – H28	1.1009	1.1013	0.4063E-03
C13 – H29	1.0999	1.0997	0.1864E-03
C13 – H30	1.1003	1.1002	0.9505E-04
C13 – H31	1.1041	1.1047	0.5789E-03
C14 – C15	1.5240	1.5244	0.4289E-03
C14 – N17	1.5154	1.5113	0.4163E-02
C14 – H32	1.0985	1.0991	0.6227E-03
C14 – H33	1.0987	1.0984	0.3923E-03
C15 – C16	1.5222	1.5122	0.1001E-01
C15 – H34	1.1033	1.1026	0.7317E-03
C15 – H35	1.1052	1.1058	0.5442E-03
C16 – O44	1.2930	1.3715	0.7848E-01
C16 – O45	1.2944	1.2448	0.4964E-01
N17 – H37	1.0400	1.0404	0.3667E-03

TABLE 3 – Comparison between the bond lengths of **1b** in the adsorbed and isolated states

Bond type	Adsorbed-phase (Å)	Gas-phase (Å)	Difference (Å)
C 1 – N18	1.3908	1.3904	0.4017E-03
C 1 – N19	1.4065	1.4044	0.2077E-02
C 1 – O44	1.2581	1.2594	0.1317E-02
C 2 – C 3	1.4460	1.4440	0.1992E-02
C 2 – N19	1.3913	1.3940	0.2698E-02
C 2 – O41	1.2875	1.2868	0.7273E-03
C 3 – C 4	1.4724	1.4691	0.3334E-02
C 3 – C 5	1.4041	1.4049	0.7395E-03
C 4 – N18	1.4099	1.4114	0.1493E-02
C 4 – O42	1.2647	1.2658	0.1105E-02
C 5 – C 6	1.4172	1.4150	0.2206E-02
C 5 – H20	1.0949	1.0948	0.1284E-03
C 6 – C 7	1.4142	1.4058	0.8383E-02
C 6 – O43	1.3574	1.3626	0.5159E-02
C 7 – C 8	1.4025	1.4086	0.6011E-02
C 7 – H21	1.0939	1.0938	0.4772E-04
C 8 – C 9	1.3944	1.3843	0.1012E-01
C 8 – H22	1.0926	1.0925	0.3404E-04
C 9 – N17	1.3524	1.3600	0.7597E-02
C 9 – H23	1.0955	1.0957	0.1545E-03
C10 – C11	1.5304	1.5304	0.3089E-04
C10 – N17	1.4706	1.4659	0.4665E-02
C10 – H24	1.1008	1.1023	0.1522E-02
C10 – H25	1.1023	1.1020	0.2524E-03
C11 – H26	1.1010	1.1016	0.5879E-03
C11 – H27	1.1012	1.1011	0.9383E-04
C11 – H28	1.1005	1.1004	0.8297E-04
C12 – C13	1.5521	1.5493	0.2762E-02
C12 – N17	1.4673	1.4558	0.1153E-01
C12 – H29	1.1028	1.1032	0.3966E-03
C12 – H30	1.1009	1.1010	0.5945E-04
C13 – C16	1.5175	1.5056	0.1195E-01
C13 – H31	1.1003	1.0999	0.3371E-03
C13 – H32	1.0998	1.0997	0.8589E-04
C14 – N18	1.4700	1.4690	0.1066E-02
C14 – H34	1.0995	1.0996	0.1139E-03
C14 – H35	1.0993	1.0994	0.3508E-04
C14 – H36	1.0959	1.0960	0.1043E-03
C15 – N19	1.4705	1.4695	0.1028E-02
C15 – H37	1.0957	1.0958	0.2062E-04
C15 – H38	1.0992	1.0993	0.1399E-03
C15 – H39	1.0991	1.0992	0.1182E-03
C16 – O45	1.2997	1.3782	0.7849E-01
C16 – O46	1.2969	1.2469	0.4998E-01
H33 – O43	1.0556	1.0483	0.7320E-02

TABLE 4 – Comparison between the bond lengths of **2b** in the adsorbed and isolated states

Bond type	Adsorbed-phase (Å)	Gas-phase (Å)	Difference (Å)
C 1 – N18	1.3954	1.3937	0.1722E-02
C 1 – N19	1.3969	1.3953	0.1561E-02
C 1 – O44	1.2625	1.2650	0.2518E-02
C 2 – C 3	1.4199	1.4119	0.7927E-02
C 2 – N19	1.4125	1.4178	0.5331E-02
C 2 – O42	1.2863	1.2916	0.5293E-02
C 3 – C 4	1.4212	1.4154	0.5751E-02
C 3 – C 5	1.4865	1.4893	0.2797E-02
C 4 – N18	1.4119	1.4168	0.4981E-02
C 4 – O41	1.2824	1.2857	0.3334E-02
C 5 – C 6	1.5493	1.5451	0.4281E-02
C 5 – C 9	1.5392	1.5396	0.3628E-03
C 5 – H20	1.1059	1.1072	0.1275E-02
C 6 – C 7	1.4819	1.4847	0.2735E-02
C 6 – O43	1.2465	1.2479	0.1384E-02
C 7 – C 8	1.3475	1.3478	0.2625E-03
C 7 – H21	1.0901	1.0904	0.2482E-03
C 8 – C 9	1.5040	1.5030	0.9136E-03
C 8 – H22	1.0941	1.0947	0.5973E-03
C 9 – N17	1.5274	1.5318	0.4435E-02
C 9 – H32	1.1028	1.1031	0.2476E-03
C10 – C11	1.5167	1.5177	0.1021E-02
C10 – N17	1.5206	1.5220	0.1451E-02
C10 – H23	1.1047	1.1081	0.3364E-02
C10 – H24	1.0995	1.1012	0.1747E-02
C11 – H25	1.0994	1.0995	0.3305E-04
C11 – H26	1.1004	1.1003	0.6180E-04
C11 – H27	1.1040	1.1046	0.6164E-03
C12 – C13	1.5214	1.5250	0.3565E-02
C12 – N17	1.5140	1.5116	0.2327E-02
C12 – H28	1.0990	1.0989	0.6711E-04
C12 – H29	1.0978	1.0982	0.3891E-03
C13 – C16	1.5163	1.5127	0.3583E-02
C13 – H30	1.1013	1.1027	0.1371E-02
C13 – H31	1.1062	1.1057	0.4424E-03
C14 – N18	1.4652	1.4642	0.9922E-03
C14 – H34	1.1003	1.1009	0.5287E-03
C14 – H35	1.0995	1.1002	0.6535E-03
C14 – H36	1.0969	1.0971	0.1871E-03
C15 – N19	1.4657	1.4640	0.1685E-02
C15 – H37	1.0996	1.1003	0.7057E-03
C15 – H38	1.1004	1.1008	0.4021E-03
C15 – H39	1.0966	1.0968	0.1291E-03
C16 – O45	1.2938	1.3713	0.7751E-01
C16 – O46	1.2928	1.2446	0.4814E-01
N17 – H33	1.0402	1.0403	0.8908E-04

Angles

TABLE 5 – Comparison between the angles of **1a** in the adsorbed and isolated states

Angle	Adsorbed-phase (°)	Gas-phase (°)	Difference (°)
C 1 – C 6 – C 5	113.9241	113.7006	0.22
C 1 – O41 – C 5	106.7144	106.5737	0.14
C 1 – O41 – C 6	110.2590	110.2936	0.03
C 1 – O42 – C 5	106.0650	106.2389	0.17
C 1 – O42 – C 6	109.2761	109.3492	0.07
C 1 – O42 – O41	110.5028	110.5911	0.08
C 2 – O39 – C 3	126.3706	126.4905	0.11
C 2 – O42 – C 3	118.1063	118.0817	0.02
C 2 – O42 – O39	115.4663	115.3605	0.10
C 3 – C 4 – C 2	119.1885	119.1462	0.04
C 3 – C 7 – C 2	125.1332	125.2018	0.06
C 3 – C 7 – C 4	115.5059	115.4480	0.05
C 4 – O40 – C 3	125.2631	125.5258	0.26
C 4 – O41 – C 3	116.6869	116.8496	0.16
C 4 – O41 – O40	117.9734	117.5534	0.42
C 5 – H18 – C 1	109.2268	109.2139	0.01
C 5 – H19 – C 1	109.5002	109.5951	0.09
C 5 – H19 – H18	109.4368	109.4039	0.03
C 5 – H20 – C 1	109.7675	109.7632	0.00
C 5 – H20 – H18	109.3869	109.3318	0.05
C 5 – H20 – H19	109.5086	109.5185	0.00
C 6 – H21 – C 1	110.5784	110.4995	0.07
C 6 – H22 – C 1	109.5924	109.5311	0.06
C 6 – H22 – H21	109.1183	109.1069	0.01
C 6 – H23 – C 1	109.1613	109.2668	0.10
C 6 – H23 – H21	108.9218	109.0059	0.08
C 6 – H23 – H22	109.4502	109.4128	0.03
C 7 – C 8 – C 3	132.6994	133.1778	0.47
C 7 – H24 – C 3	113.0388	112.7360	0.30
C 7 – H24 – C 8	114.2617	114.0863	0.17
C 8 – C 9 – C 7	117.2070	117.0091	0.19
C 8 – O43 – C 7	125.2079	125.0397	0.16
C 8 – O43 – C 9	117.5787	117.9499	0.37
C 9 – C10 – C 8	123.7737	124.3903	0.61
C 9 – H25 – C 8	116.9710	116.7533	0.21
C 9 – H25 – C10	119.2452	118.8559	0.38
C10 – C11 – C 9	120.5950	120.9806	0.38
C10 – H26 – C 9	118.0189	117.7167	0.30
C10 – H26 – C11	121.3514	121.3024	0.04
C11 – N17 – C10	126.8038	127.0497	0.24
C11 – H27 – C10	118.9712	118.8983	0.07
C11 – H27 – N17	114.2152	114.0503	0.16
C12 – N17 – C13	111.3117	112.1114	0.79
C12 – H28 – C13	110.6834	110.5607	0.12
C12 – H28 – N17	107.2817	107.4974	0.21
C12 – H29 – C13	111.5032	110.8117	0.69
C12 – H29 – N17	108.6818	108.4747	0.20
C12 – H29 – H28	107.1941	107.1968	0.00
C13 – H30 – C12	110.4865	110.7858	0.29
C13 – H31 – C12	110.2787	110.1204	0.15
C13 – H31 – H30	108.1862	108.2466	0.06
C13 – H32 – C12	110.4214	110.5230	0.10
C13 – H32 – H30	108.6100	108.5622	0.04
C13 – H32 – H31	108.7973	108.5330	0.26
C14 – N17 – C15	110.8588	111.6744	0.81
C14 – H33 – C15	109.9351	109.4871	0.44
C14 – H33 – N17	108.7978	108.8639	0.06
C14 – H34 – C15	109.9241	109.8126	0.11
C14 – H34 – N17	109.2329	108.9573	0.27
C14 – H34 – H33	108.0344	107.9649	0.06
C15 – C16 – C14	109.6768	110.3842	0.70
C15 – H35 – C14	110.3046	109.4175	0.88
C15 – H35 – C16	108.8169	107.7176	1.09
C15 – H36 – C14	109.2719	108.9623	0.30
C15 – H36 – C16	108.6851	110.5497	1.86
C15 – H36 – H35	110.0606	109.7931	0.26
C16 – O44 – C15	116.3398	111.9072	4.43
C16 – O45 – C15	116.9552	125.3878	8.43
C16 – O45 – O44	126.6756	122.6485	4.02
N17 – C12 – C11	122.8684	121.8433	1.02
N17 – C14 – C11	120.4156	120.6533	0.23
N17 – C14 – C12	116.7135	117.5035	0.78
O41 – C 4 – C 1	117.7962	118.0010	0.20
O42 – C 2 – C 1	117.8627	117.9499	0.08
O43 – H37 – C 8	108.3562	108.1645	0.19

TABLE 6 – Comparison between the angles of **2a** in the adsorbed and isolated states

Angle	Adsorbed-phase (°)	Gas-phase (°)	Difference (°)
C 1 – H18 – C 2	109.8339	109.8574	0.02
C 1 – H19 – C 2	109.3320	109.3646	0.03
C 1 – H19 – H18	109.3799	109.3730	0.00
C 1 – H20 – C 2	109.4589	109.4730	0.01
C 1 – H20 – H18	109.4359	109.4209	0.01
C 1 – H20 – H19	109.3862	109.3375	0.04
C 2 – C 3 – C 1	113.4184	112.7449	0.67
C 2 – O39 – C 1	106.0758	106.1818	0.10
C 2 – O39 – C 3	110.3269	110.4602	0.13
C 2 – O40 – C 1	106.1282	106.1117	0.01
C 2 – O40 – C 3	110.3554	110.6751	0.31
C 2 – O40 – O39	110.3823	110.5036	0.12
C 3 – H21 – C 2	109.1507	109.1375	0.01
C 3 – H22 – C 2	109.1139	108.9386	0.17
C 3 – H22 – H21	109.2782	109.1269	0.15
C 3 – H23 – C 2	111.0437	111.1368	0.09
C 3 – H23 – H21	109.2600	109.4261	0.16
C 3 – H23 – H22	108.9708	109.0460	0.07
C 4 – O40 – C 5	116.5993	116.5423	0.05
C 4 – O42 – C 5	125.3756	125.9873	0.61
C 4 – O42 – O40	117.8349	117.3000	0.53
C 5 – C 6 – C 4	121.3501	121.7211	0.37
C 5 – C 7 – C 4	119.6842	119.6346	0.04
C 5 – C 7 – C 6	118.2742	117.8781	0.39
C 6 – O39 – C 5	116.8296	116.7904	0.03
C 6 – O41 – C 5	124.7320	125.1606	0.42
C 6 – O41 – O39	118.2761	117.8908	0.38
C 7 – C 8 – C 5	115.2208	115.2590	0.03
C 7 – C11 – C 5	116.1069	116.4059	0.29
C 7 – C11 – C 8	102.0341	101.9155	0.11
C 7 – H24 – C 5	107.6288	107.2389	0.38
C 7 – H24 – C 8	105.8164	105.8730	0.05
C 7 – H24 – C11	109.4905	109.6172	0.12
C 8 – C 9 – C 7	107.6558	107.8968	0.24
C 8 – O43 – C 7	125.6996	125.9126	0.21
C 8 – O43 – C 9	126.6360	126.1784	0.45
C 9 – C10 – C 8	110.0323	110.0391	0.00
C 9 – H25 – C 8	122.8635	122.8615	0.00
C 9 – H25 – C10	127.0891	127.0845	0.00
C10 – C11 – C 9	111.2178	110.8952	0.32
C10 – H26 – C 9	125.8462	125.7797	0.06
C10 – H26 – C11	122.7465	123.0535	0.30
C11 – C10 – C 7	105.8589	106.1661	0.30
C11 – N17 – C 7	113.4057	113.3933	0.01
C11 – N17 – C10	112.3750	112.5426	0.16
C11 – H36 – C 7	108.7230	108.3445	0.37
C11 – H36 – C10	109.5043	109.5014	0.00
C11 – H36 – N17	106.9145	106.8111	0.10
C12 – N17 – C13	112.2401	112.0752	0.16
C12 – H27 – C13	113.0160	113.2684	0.25
C12 – H27 – N17	106.0002	105.9454	0.05
C12 – H28 – C13	111.2239	110.9976	0.22
C12 – H28 – N17	105.2018	105.2824	0.08
C12 – H28 – H27	108.7204	108.8357	0.11
C13 – H29 – C12	112.1318	111.8915	0.24
C13 – H30 – C12	108.3023	108.1658	0.13
C13 – H30 – H29	107.6160	107.7530	0.13
C13 – H31 – C12	111.8417	111.8644	0.02
C13 – H31 – H29	109.2509	109.4787	0.22
C13 – H31 – H30	107.4979	107.4961	0.00
C14 – N17 – C15	110.4227	110.6959	0.27
C14 – H32 – C15	110.5097	110.6160	0.10
C14 – H32 – N17	107.8201	107.9900	0.16
C14 – H33 – C15	112.3375	111.9169	0.42
C14 – H33 – N17	107.2541	107.1216	0.13
C14 – H33 – H32	108.3307	108.3443	0.01
C15 – C16 – C14	112.8331	110.8760	1.95
C15 – H34 – C14	112.0681	112.4281	0.35
C15 – H34 – C16	106.3284	108.0509	1.72
C15 – H35 – C14	111.4069	111.3019	0.10
C15 – H35 – C16	107.2766	107.5332	0.25
C15 – H35 – H34	106.5403	106.4064	0.13
C16 – O44 – C15	115.3236	111.0443	4.27
C16 – O45 – C15	117.1176	125.1810	8.06
C16 – O45 – O44	127.5531	123.7738	3.77
N17 – C12 – C11	112.9086	112.5349	0.37
N17 – C14 – C11	113.0289	112.9458	0.08
N17 – C14 – C12	110.9787	110.5172	0.46
N17 – H37 – C11	105.5626	105.5940	0.03
N17 – H37 – C12	106.7059	107.0399	0.33
N17 – H37 – C14	107.1284	107.8004	0.67
O39 – C 6 – C 2	115.5538	115.1130	0.44
O40 – C 4 – C 2	116.0464	115.7722	0.27

TABLE 7 – Comparison between the angles of **1b** in the adsorbed and isolated states

Angle	Adsorbed-phase (°)	Gas-phase (°)	Difference (°)
C 1 – N19 – N18	116.6493	116.5921	0.05
C 1 – O44 – N18	121.3672	121.3328	0.03
C 1 – O44 – N19	121.9836	122.0753	0.09
C 2 – N19 – C 3	118.3025	118.1901	0.11
C 2 – O41 – C 3	125.0341	125.3486	0.31
C 2 – O41 – N19	116.6635	116.4614	0.20
C 3 – C 4 – C 2	119.3514	119.4919	0.14
C 3 – C 5 – C 2	125.5226	125.4711	0.05
C 3 – C 5 – C 4	115.1260	115.0371	0.08
C 4 – N18 – C 3	116.6792	116.6574	0.02
C 4 – O42 – C 3	123.5068	123.7482	0.24
C 4 – O42 – N18	119.8141	119.5945	0.21
C 5 – C 6 – C 3	133.4657	133.6173	0.15
C 5 – H20 – C 3	112.2826	112.2572	0.02
C 5 – H20 – C 6	114.2516	114.1255	0.12
C 6 – C 7 – C 5	117.0580	116.7588	0.29
C 6 – O43 – C 5	124.8777	125.1478	0.27
C 6 – O43 – C 7	118.0641	118.0935	0.02
C 7 – C 8 – C 6	124.5759	124.4154	0.16
C 7 – H21 – C 6	116.4597	116.7615	0.30
C 7 – H21 – C 8	118.9624	118.8232	0.13
C 8 – C 9 – C 7	121.0485	120.8412	0.20
C 8 – H22 – C 7	117.8021	117.7684	0.03
C 8 – H22 – C 9	121.1444	121.3893	0.24
C 9 – N17 – C 8	126.8062	127.1017	0.29
C 9 – H23 – C 8	118.8508	118.8749	0.02
C 9 – H23 – N17	114.3430	114.0220	0.32
C10 – N17 – C11	112.4138	112.1100	0.30
C10 – H24 – C11	110.5073	110.5526	0.04
C10 – H24 – N17	107.2462	107.5220	0.27
C10 – H25 – C11	110.6667	110.7839	0.11
C10 – H25 – N17	108.4395	108.4715	0.03
C10 – H25 – H24	107.3729	107.2153	0.15
C11 – H26 – C10	110.9847	110.7832	0.20
C11 – H27 – C10	109.6818	110.1564	0.47
C11 – H27 – H26	108.2257	108.2337	0.00
C11 – H28 – C10	110.8688	110.5076	0.36
C11 – H28 – H26	108.6120	108.5497	0.06
C11 – H28 – H27	108.3883	108.5400	0.15
C12 – N17 – C13	111.1861	111.8132	0.62
C12 – H29 – C13	109.9132	109.3320	0.58
C12 – H29 – N17	108.6070	108.9850	0.37
C12 – H30 – C13	110.1482	109.7652	0.38
C12 – H30 – N17	108.8363	108.8924	0.05
C12 – H30 – H29	108.0770	107.9700	0.10
C13 – C16 – C12	110.5887	110.0341	0.55
C13 – H31 – C12	109.3559	109.3402	0.01
C13 – H31 – C16	109.1479	107.7161	1.43
C13 – H32 – C12	108.6325	109.1999	0.56
C13 – H32 – C16	109.0759	110.7411	1.66
C13 – H32 – H31	110.0304	109.7858	0.24
C14 – H34 – N18	109.5678	109.6132	0.04
C14 – H35 – N18	109.5089	109.5506	0.04
C14 – H35 – H34	108.2461	108.2376	0.00
C14 – H36 – N18	107.2668	107.1729	0.09
C14 – H36 – H34	111.0788	111.0781	0.00
C14 – H36 – H35	111.1578	111.1758	0.01
C15 – H37 – N19	107.5435	107.5346	0.00
C15 – H38 – N19	109.4492	109.4806	0.03
C15 – H38 – H37	111.0022	111.0248	0.02
C15 – H39 – N19	109.4347	109.4631	0.02
C15 – H39 – H37	111.0238	111.0637	0.03
C15 – H39 – H38	108.3686	108.2577	0.11
C16 – O45 – C13	116.1769	112.0316	4.14
C16 – O46 – C13	117.4975	125.2202	7.72
C16 – O46 – O45	126.2748	122.6836	3.59
N17 – C10 – C 9	121.4035	121.8612	0.45
N17 – C12 – C 9	121.0890	120.6467	0.44
N17 – C12 – C10	117.4523	117.4918	0.03
N18 – C 4 – C 1	124.7973	124.7991	0.00
N18 – C14 – C 1	115.7709	115.8433	0.07
N18 – C14 – C 4	119.4318	119.3576	0.07
N19 – C 2 – C 1	124.2198	124.2689	0.04
N19 – C15 – C 1	117.9919	118.1105	0.11
N19 – C15 – C 2	117.7883	117.6207	0.16
O43 – H33 – C 6	107.9607	107.7747	0.18

TABLE 8 – Comparison between the angles of **2b** in the adsorbed and isolated states

Angle	Adsorbed-phase (°)	Gas-phase (°)	Difference (°)
C 1 – N19 – N18	117.1647	117.0628	0.10
C 1 – O44 – N18	121.4641	121.5235	0.05
C 1 – O44 – N19	121.3546	121.3983	0.04
C 2 – N19 – C 3	116.0323	115.9145	0.11
C 2 – O42 – C 3	123.7280	124.2988	0.57
C 2 – O42 – N19	120.1917	119.7471	0.44
C 3 – C 4 – C 2	122.7217	123.0409	0.31
C 3 – C 5 – C 2	119.7335	119.6863	0.04
C 3 – C 5 – C 4	117.4746	117.2199	0.25
C 4 – N18 – C 3	116.3705	116.3592	0.01
C 4 – O41 – C 3	122.7161	123.1069	0.39
C 4 – O41 – N18	120.8943	120.5103	0.38
C 5 – C 6 – C 3	115.4986	115.5124	0.01
C 5 – C 9 – C 3	115.4561	115.6944	0.23
C 5 – C 9 – C 6	102.2669	102.1593	0.10
C 5 – H20 – C 3	107.2763	106.9171	0.35
C 5 – H20 – C 6	105.9847	106.1900	0.20
C 5 – H20 – C 9	109.9274	109.9607	0.03
C 6 – C 7 – C 5	107.6418	107.8297	0.18
C 6 – O43 – C 5	125.8155	126.1536	0.33
C 6 – O43 – C 7	126.4793	125.9324	0.54
C 7 – C 8 – C 6	110.2678	110.2796	0.01
C 7 – H21 – C 6	122.5619	122.6588	0.09
C 7 – H21 – C 8	127.1624	127.0583	0.10
C 8 – C 9 – C 7	111.0887	110.8177	0.27
C 8 – H22 – C 7	125.8226	125.9204	0.09
C 8 – H22 – C 9	122.8284	122.9800	0.15
C 9 – C 8 – C 5	106.0872	106.4295	0.34
C 9 – N17 – C 5	112.7430	113.0850	0.34
C 9 – N17 – C 8	112.7170	112.3279	0.38
C 9 – H32 – C 5	109.4144	109.1258	0.28
C 9 – H32 – C 8	109.4644	109.6262	0.16
C 9 – H32 – N17	106.3954	106.2200	0.17
C10 – N17 – C11	112.6972	112.1480	0.54
C10 – H23 – C11	113.2896	113.0735	0.21
C10 – H23 – N17	105.7263	106.0092	0.28
C10 – H24 – C11	110.7327	110.8857	0.15
C10 – H24 – N17	105.5347	105.3602	0.17
C10 – H24 – H23	108.4189	108.9571	0.53
C11 – H25 – C10	111.9781	111.5803	0.39
C11 – H26 – C10	108.0814	108.2756	0.19
C11 – H26 – H25	107.8318	107.8088	0.02
C11 – H27 – C10	111.8954	111.9832	0.08
C11 – H27 – H25	109.4392	109.5746	0.13
C11 – H27 – H26	107.4185	107.4343	0.01
C12 – N17 – C13	110.2764	110.6884	0.41
C12 – H28 – C13	111.1113	110.6645	0.44
C12 – H28 – N17	108.0830	108.0074	0.07
C12 – H29 – C13	111.6566	111.8886	0.23
C12 – H29 – N17	107.0502	107.1498	0.09
C12 – H29 – H28	108.5076	108.2856	0.22
C13 – C16 – C12	112.4832	110.8478	1.63
C13 – H30 – C12	112.9418	112.4880	0.45
C13 – H30 – C16	107.3792	108.0130	0.63
C13 – H31 – C12	111.0772	111.3069	0.22
C13 – H31 – C16	106.0232	107.5351	1.51
C13 – H31 – H30	106.5045	106.4033	0.10
C14 – H34 – N18	110.0337	110.0808	0.04
C14 – H35 – N18	109.5369	109.6884	0.15
C14 – H35 – H34	108.1065	107.8579	0.24
C14 – H36 – N18	107.1536	107.1886	0.03
C14 – H36 – H34	110.8519	110.9056	0.05
C14 – H36 – H35	111.1580	111.1270	0.03
C15 – H37 – N19	109.5364	109.6315	0.09
C15 – H38 – N19	109.9876	110.1249	0.13
C15 – H38 – H37	108.0040	107.8109	0.19
C15 – H39 – N19	107.2488	107.1800	0.06
C15 – H39 – H37	111.1469	111.1410	0.00
C15 – H39 – H38	110.9174	110.9603	0.04
C16 – O45 – C13	114.9212	111.0628	3.85
C16 – O46 – C13	117.2463	125.1210	7.87
C16 – O46 – O45	127.8195	123.8157	4.00
N17 – C10 – C 9	112.5449	112.4941	0.05
N17 – C12 – C 9	113.2382	113.0625	0.17
N17 – C12 – C10	109.7166	110.4360	0.71
N17 – H33 – C 9	105.9240	105.5559	0.36
N17 – H33 – C10	107.3977	107.1742	0.22
N17 – H33 – C12	107.6679	107.7118	0.04
N18 – C 4 – C 1	123.5005	123.4027	0.09
N18 – C14 – C 1	116.6319	116.4861	0.14
N18 – C14 – C 4	119.8648	120.1086	0.24
N19 – C 2 – C 1	123.7942	123.8090	0.01
N19 – C15 – C 1	116.3091	116.1454	0.16
N19 – C15 – C 2	119.8945	120.0443	0.14

Molecular orbitals

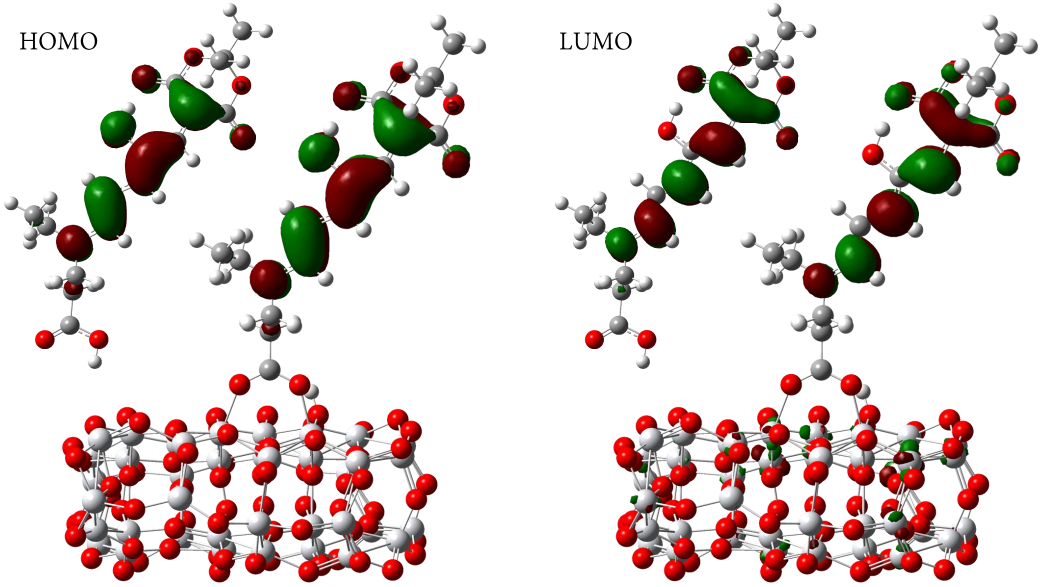

FIGURE 1 – Electronic density of the HOMO and LUMO of **1a** in the gas and adsorbed phases, obtained with the CAM-B3LYP functional. An isovalue of 0.03 e/Å^3 is used to plot the isosurfaces.

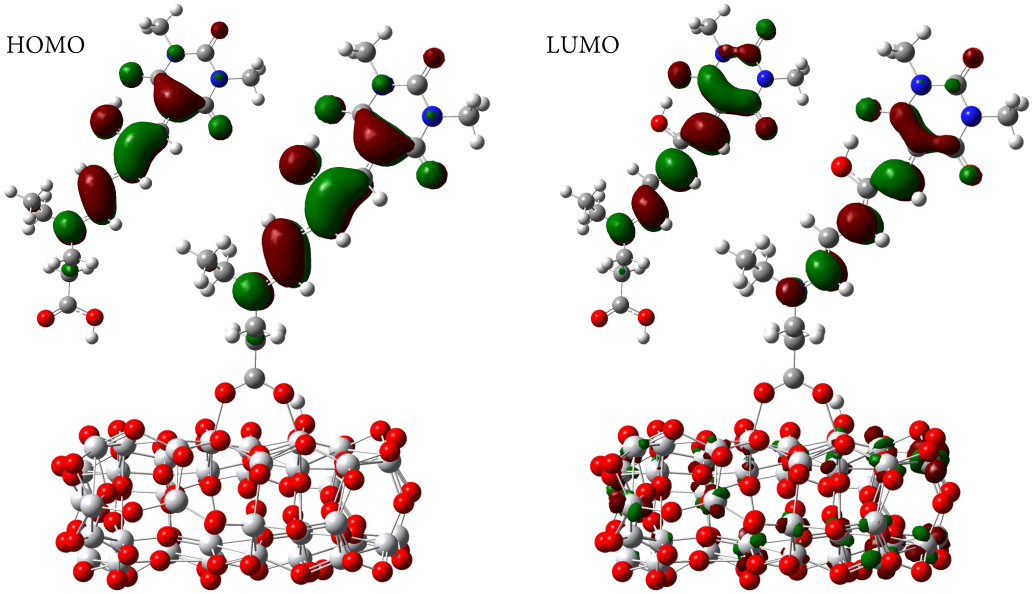

FIGURE 2 – Electronic density of the HOMO and LUMO of **1b** in the gas and adsorbed phases, obtained with the CAM-B3LYP functional. An isovalue of 0.03 e/Å^3 is used to plot the isosurfaces.

TABLE 9 – CAM-B3LYP/6-31G(d) optimized structure of the bare TiO_2 finite cluster

Atom	x (Å)	y (Å)	z (Å)
O	0.475673	-1.421381	1.412151
O	2.648592	-3.306103	4.004443
Ti	-0.267332	-5.356090	2.338208
O	-1.442554	-4.493593	0.797034
O	0.124414	-3.581967	2.633464
Ti	1.720898	-2.386764	2.716754
Ti	-0.683080	-2.718296	0.821834
Ti	-2.788779	-5.650069	1.027544
O	1.056658	-5.611238	0.926652
O	-1.916624	-6.141190	2.545348
O	0.855563	-6.492764	3.188946
O	2.749336	-2.860730	-2.080360
Ti	1.465666	-4.022590	-1.924709
O	2.953222	-3.043500	1.623302
O	2.267439	-5.754843	-1.749200
O	5.519217	-3.180473	3.136604
O	-2.996599	2.903237	-0.016236
O	-0.080650	1.190207	2.105456
Ti	-3.196290	-0.962905	0.509632
O	-4.808068	0.085047	-0.496921
O	-4.135883	-2.319521	-0.505674
Ti	-5.016095	-3.869364	-0.578089
Ti	-5.642570	-1.249084	-1.530955
Ti	-3.757256	1.588646	-1.117449
O	-2.349417	0.481286	0.068013
O	-2.312255	-2.033800	1.890562
O	0.163055	1.262603	-3.761756
O	2.550442	-0.241395	-3.069605
O	0.112751	1.126568	-0.292385
O	2.070559	-0.497409	-0.638808
Ti	-0.798289	-2.381182	-2.116032
O	-2.042542	-1.107332	-4.719399
O	-2.424129	-3.080041	-2.817745
Ti	-3.165449	-4.685901	-3.281515
Ti	-3.435823	-2.110408	-4.439657
Ti	-1.421867	0.544195	-3.914785
O	0.303393	-3.455931	-3.143653
O	-1.726281	-1.936929	-0.405863
O	-0.443300	-0.718179	-2.473567
O	0.399120	-3.054525	-0.699210
Ti	3.887729	0.172391	2.747180
O	2.650873	1.404883	1.288432
Ti	1.171146	0.326313	0.969177
O	2.243152	-0.621456	2.908041
O	4.917445	-0.576197	3.860860
Ti	5.855125	2.854968	2.581585
O	4.967118	4.101281	1.777276
Ti	3.280152	3.141541	1.374301
O	6.678595	1.585635	1.392102
O	4.348696	2.020251	2.989737
O	7.410227	2.616415	3.560197
Ti	5.905570	-1.050388	-0.214185
O	4.814524	0.355425	-1.331518
O	7.524822	-0.097015	-0.730899
Ti	7.868006	1.453178	-0.132656
Ti	5.205095	2.107082	-1.576088
Ti	3.330129	-1.130131	-1.719604
O	4.906109	-0.616518	1.399668
O	5.002422	-2.110954	-1.156324
O	6.851957	-2.031650	1.036823
O	7.614930	-0.408130	3.141267
Ti	6.173474	-1.557073	2.598429
Ti	8.109562	1.203782	2.659453
Ti	0.918231	4.571014	1.266898
O	-1.808638	6.193885	0.390671
O	-0.700759	3.697799	0.863194
Ti	-1.166956	1.844560	0.924089
Ti	-2.303172	4.542055	-0.429195
Ti	-0.380077	7.103895	0.073543
O	0.802106	6.396485	1.241738
O	2.024754	3.905797	2.489323
Ti	2.940043	3.678160	-1.921732
O	1.709366	4.448751	-3.211952
O	1.942827	2.167497	-1.889423
Ti	1.166369	0.650523	-2.292915
Ti	1.830015	6.058890	-2.644029
O	4.342151	3.030028	-2.863935
O	2.071778	4.015340	0.061060
O	3.196389	5.671685	-1.687893
O	4.200352	2.944260	-0.390460
O	3.674271	-5.704912	2.504924
Ti	2.209479	-6.612884	1.965476
Ti	3.910259	-3.942610	2.898937
Ti	1.281279	-6.774467	-0.734945
O	-4.522615	-4.732508	-2.051757
O	-4.441830	-4.837747	0.850132
O	-2.492580	-6.813010	-0.284040
Ti	-1.306673	-6.799255	-1.701281
O	-0.212686	-5.535301	-1.298354
O	0.078756	-7.951882	-1.483477
O	2.283624	-7.712689	0.580587
O	-6.462112	-2.785029	-1.000729
O	-2.183373	-6.180209	-3.209225
O	-3.652036	-3.928027	-4.808635
O	6.978283	2.537596	-1.245411
O	9.162748	1.452766	1.221913
O	-0.661512	8.564822	-1.029090
O	1.069545	7.633427	-3.486598
O	0.238465	6.318531	-1.512381
O	-1.859536	6.863995	-3.372489
Ti	-0.458013	7.715666	-2.630116
O	-3.594849	5.359501	-1.443871
O	-1.505470	4.311643	-2.003067
O	-3.470987	4.105791	-4.120876
Ti	-2.701034	5.264314	-2.975236
O	-4.711882	2.493864	-2.180323
O	-2.360732	1.659364	-4.976163
O	-2.649291	1.240771	-2.606469
Ti	-5.597462	-0.316831	-4.209656
O	-5.104580	1.331600	-4.573894
Ti	-3.683964	2.313063	-3.922903
O	-6.742881	-0.565774	-2.779790
O	-4.910414	-1.452551	-5.382186
O	-4.378678	-1.139352	-3.016535