Supporting information for "Probing the photoabsorption features and electronic excited states of propylene oxide: an experimental and theoretical study"

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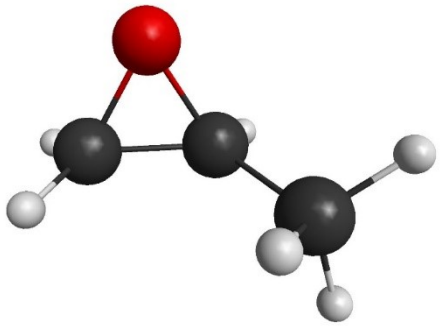
Fig S1: Optimized Molecular Geometry for propylene oxide, obtained at the DFT/CAMB3LYP/aug-cc-pVQZ level of theory



Coordinates of all atoms (in angstroms)

	X	Y	Z
O	0.7970503152	-0.7448708031	0.0511291443
C	-0.2278454818	0.0899913838	-0.4722727101
C	0.9594960083	0.6635519053	0.1508161175
C	-1.5528167097	0.0417541032	0.2222297771
H	-0.2667460597	0.0903506005	-1.5572579110
H	1.7477223589	1.0818723434	-0.4633479399
H	0.8879908407	1.0641641306	1.1553180800
H	-2.1675383909	0.8932029863	-0.0686876075
H	-2.0896306318	-0.8681891712	-0.0424690945
H	-1.4196825791	0.0591724610	1.3019421942

Table S1: calculated vertical excitation energies (in eV) and oscillator strengths (f_0) obtained at TDDFT/CAMB3LYP/aug-cc-pVQZ level of theory. It is also shown the assignments obtained after the analysis of the natural transition orbitals, as shown in the main manuscript.

	Energy (eV)	f_0	Sym	Major assignment	NTO assignment
1	7.1586	0.00934	A	HOMO->LUMO (71%), HOMO->L+3 (10%)	0.99 nO -> 3s
2	7.4879	0.01531	A	HOMO->LUMO (10%), HOMO->L+3 (39%), HOMO->L+6 (29%)	0.98 nO-> 3p''
3	7.5828	0.01466	A	HOMO->L+2 (79%)	0.98 nO -> 3p'
4	7.7406	0.01894	A	HOMO->L+1 (76%)	0.98 nO-> 3p
5	7.8752	0.00638	A	H-1->LUMO (83%)	0.97 σ_CO -> 3s
6	8.3159	0.00962	A	H-1->L+2 (57%), H-1->L+3 (15%)	0.96 σ_CO -> 3p'
7	8.3637	0.03531	A	H-1->L+2 (24%), H-1->L+3 (35%), H-1->L+6 (14%)	0.92 σ_CO -> 3p' '
8	8.4226	0.01483	A	H-1->L+1 (11%), HOMO->L+4 (33%), HOMO->L+7 (15%)	0.83 nO-> 3d
9	8.4650	0.00241	A	H-1->L+1 (64%)	0.88 σ_CO -> 3p
10	8.5661	0.00438	A	HOMO->L+3 (10%), HOMO->L+4 (31%), HOMO->L+6 (11%), HOMO->L+7 (15%)	0.96 nO-> 3d'
11	8.6015	0.01741	A	HOMO->L+3 (21%), HOMO->L+5 (16%), HOMO->L+6 (23%)	0.98 nO-> 3d''
12	8.6701	0.00356	A	HOMO->L+5 (62%), HOMO->L+6 (13%)	0.98 nO--> 3d'''
13	9.0402	0.00680	A	HOMO->L+8 (67%)	0.98 nO-> ryd-like (d)
14	9.1860	0.02467	A	H-1->L+4 (68%)	0.89 σ_CO ->3d
15	9.2352	0.00798	A	HOMO->L+7 (22%), HOMO->L+17 (12%)	0.88 nO-> 4d
16	9.2929	0.01287	A	H-1->L+3 (26%), H-1->L+5 (11%), H-1->L+6 (44%)	0.92 σ_CO -> 3d/p
17	9.3836	0.00710	A	HOMO->L+9 (31%), HOMO->L+8 (8%), HOMO->L+11 (8%), HOMO->L+7 (7%), HOMO->L+17 (7%),	0.89 nO --> 5s
18	9.3954	0.00815	A	H-1->L+5 (70%)	0.93 σ_CO -> 3d
19	9.4850	0.00674	A	HOMO->L+9 (14%), HOMO->L+10 (50%)	0.90 nO-> 5p
20	9.5425	0.03394	A	H-2->LUMO (20%), H-1->L+7 (49%)	0.64 σ_CO -> 3d + 0.22 σ_CH/nO->3s
21	9.5886	0.00330	A	H-2->LUMO (31%), HOMO->L+11 (16%)	0.53 nO-> ryd-like + 0.35 σ_CH/nO-> 3s
22	9.6530	0.03482	A	H-2->LUMO (25%), H-1->L+7 (20%), HOMO->L+11 (19%)	0.47 nO-> 5d? + 0.27 σ_CH/nO->4s +0.22 σ_CO -> 3d
23	9.7004	0.01050	A	HOMO->L+11 (23%), HOMO->L+13 (12%), HOMO->L+15 (12%), HOMO->L+18 (12%)	0.93 nO -> 6s
24	9.7968	0.00577	A	H-3->LUMO (10%), HOMO->L+11 (13%), HOMO->L+12 (34%), HOMO->L+13 (18%)	0.83 nO -> ryd-like / σ*_CH
25	9.8233	0.00447	A	H-1->L+8 (73%)	0.94 σ_CO -> ryd-like (d)
26	9.8998	0.02423	A	H-3->LUMO (56%)	0.63 σ_CC/nO --> 3s + 0.18 nO-> ryd d like
27	10.0472	0.01307	A	HOMO->L+12 (27%), HOMO->L+13 (23%)	0.87 nO-> ryd-like
28	10.0734	0.01199	A	H-1->L+9 (43%), H-1->L+10 (11%)	0.91 σ_CO -> ryd-like / σ*_CH
29	10.0950	0.07678	A	H-2->L+1 (20%), H-2->L+2 (43%)	0.75 σ_CH/nO -> 3p
30	10.1751	0.00266	A	H-2->L+1 (20%), H-2->L+3 (13%), H-1->L+10 (11%)	0.52 σ_CH/nO -> 3p' + 0.30 σ_CO->σ*_CH
31	10.2138	0.00932	A	H-2->L+1 (14%), H-2->L+2 (14%), H-1->L+10 (32%)	0.59 σ_CO -> ryd-like/σ*_CH + 0.32 σ_CH/nO -> σ*'_CH/ryd-like (p)
32	10.2658	0.01171	A	HOMO->L+14 (40%), HOMO->L+20 (10%)	0.75 nO -> Ryd-like / σ*_CO
33	10.2813	0.00814	A	H-2->L+2 (10%), H-2->L+3 (14%), HOMO->L+15 (18%), HOMO->L+16 (16%)	0.50 nO -> ryd d / σ*_CH + 0.30 σ_CH/nO -> 3p
34	10.3118	0.01121	A	H-2->L+3 (22%), HOMO->L+16 (19%)	0.42 nO -> rydberg/σ*_CO + 0.32 σ_CH/nO -> 3p
35	10.3218	0.00232	A	H-1->L+11 (29%), H-1->L+12 (10%)	0.78 σ_CO -> σ*_CH / ryd-like
36	10.3838	0.04231	A	H-3->L+2 (46%), H-3->L+3 (6%), HOMO->L+13 (3%), HOMO->L+19 (3%), HOMO->L+15 (3%), H-1->L+15 (3%), H-1->L+10 (3%)	0.61 σ_CC/nO -> 3p' + 0.18 nO -> ryd-like
37	10.4223	0.00973	A	H-3->L+2 (27%), H-3->L+3 (14%)	0.57 σ_CC/nO -> 3p'/3p'' + 0.21 σ_CO -> ryd-like
38	10.4804	0.00306	A	H-1->L+11 (21%), H-1->L+14 (10%), H-1->L+15 (13%), H-3->L+1 (6%), H-3->L+3 (8%)	0.71 σ_CO -> ryd-like + 0.19 σ_CC/nO -> 3p
39	10.4986	0.00519	A	H-3->L+1 (27%), HOMO->L+16 (15%), HOMO->L+13 (9%), HOMO->L+19 (9%), HOMO->L+17 (8%), HOMO->L+18 (6%)	0.55 nO -> ryd-like + 0.36 σ_CC/nO -> 3p
40	10.5158	0.01438	A	H-3->L+1 (42%), H-3->L+3 (12%)	0.65 σ_CC/nO -> 3p'' + 0.19 nO -> ryd-like

Table S2. calculated vertical excitation energies (in eV) and oscillator strengths (f_0) obtained at TDDFT/CAMB3LYP/aug-cc-pVTZ level of theory.

	Energy (eV)	f_0	sym	Major assignment
1	7.1581	0.00965	A	HOMO->LUMO (73%), HOMO->L+3 (9%)
2	7.4966	0.01483	A	HOMO->LUMO (10%), HOMO->L+3 (40%), HOMO->L+6 (32%)
3	7.5849	0.01535	A	HOMO->L+2 (81%)
4	7.7451	0.01928	A	HOMO->L+1 (78%)
5	7.8783	0.00651	A	H-1->LUMO (85%)
6	8.3246	0.00858	A	H-1->L+2 (66%), H-1->L+3 (12%)
7	8.3785	0.03746	A	H-1->L+2 (18%), H-1->L+3 (39%), H-1->L+6 (17%)
8	8.4382	0.01588	A	H-1->L+1 (16%), HOMO->L+4 (31%), HOMO->L+7 (17%)
9	8.4750	0.00228	A	H-1->L+1 (61%)
10	8.5937	0.00542	A	HOMO->L+4 (36%), HOMO->L+7 (14%), HOMO->L+17 (10%)
11	8.6268	0.01814	A	HOMO->L+3 (26%), HOMO->L+5 (16%), HOMO->L+6 (27%)
12	8.7075	0.00380	A	HOMO->L+5 (66%), HOMO->L+6 (11%)
13	9.2027	0.02072	A	H-1->L+4 (22%), HOMO->L+8 (40%)
14	9.2188	0.01753	A	H-1->L+4 (55%), HOMO->L+8 (16%)
15	9.3236	0.01290	A	H-1->L+3 (29%), H-1->L+5 (12%), H-1->L+6 (46%)
16	9.3900	0.00673	A	HOMO->L+7 (22%), HOMO->L+9 (10%), HOMO->L+10 (13%), HOMO->L+17 (13%)
17	9.4357	0.01039	A	H-1->L+5 (73%), H-1->L+6 (10%)
18	9.5478	0.01119	A	HOMO->L+8 (17%), HOMO->L+9 (28%), HOMO->L+17 (10%)
19	9.5647	0.02015	A	H-2->LUMO (63%), H-1->L+7 (11%)
20	9.6516	0.00700	A	H-1->L+7 (10%), HOMO->L+9 (18%), HOMO->L+10 (38%), HOMO->L+12 (11%)
21	9.6762	0.05257	A	H-2->LUMO (19%), H-1->L+7 (45%)
22	9.8630	0.03464	A	H-3->LUMO (16%), HOMO->L+11 (15%), HOMO->L+14 (18%)
23	9.8819	0.01075	A	H-3->LUMO (53%), HOMO->L+12 (13%)
24	9.9425	0.00682	A	HOMO->L+11 (55%), HOMO->L+14 (11%)
25	9.9946	0.00142	A	H-1->L+8 (64%)
26	10.0434	0.04312	A	H-2->L+2 (21%), HOMO->L+12 (16%), HOMO->L+13 (17%)
27	10.1184	0.04080	A	H-3->LUMO (12%), H-2->L+1 (22%), H-2->L+2 (26%)
28	10.1961	0.00322	A	H-2->L+1 (30%), H-2->L+2 (23%), H-2->L+3 (14%)
29	10.2316	0.00929	A	H-1->L+9 (39%), H-1->L+10 (17%)
30	10.2970	0.00376	A	H-2->L+3 (16%), HOMO->L+12 (16%), HOMO->L+13 (13%)
31	10.3054	0.03364	A	H-2->L+3 (22%), HOMO->L+13 (19%)
32	10.3661	0.01929	A	H-3->L+2 (12%), H-2->L+3 (10%), H-1->L+9 (15%), H-1->L+10 (32%)
33	10.3996	0.03183	A	H-3->L+2 (67%)
34	10.4561	0.00472	A	H-3->L+1 (24%), H-3->L+3 (29%), H-3->L+6 (13%)
35	10.5137	0.01024	A	H-3->L+1 (50%), H-3->L+3 (22%)
36	10.5593	0.01215	A	H-1->L+11 (20%), H-1->L+12 (26%), H-1->L+14 (18%)
37	10.5932	0.00740	A	HOMO->L+14 (23%), HOMO->L+16 (13%), HOMO->L+20 (18%)
38	10.6303	0.00563	A	HOMO->L+15 (34%), HOMO->L+16 (36%)
39	10.6830	0.01500	A	H-4->LUMO (39%)
40	10.7063	0.00134	A	H-1->L+11 (46%), H-1->L+14 (13%)

Table S3. calculated vertical excitation energies (in eV) and oscillator strengths (f_0) obtained at TDDFT/B3LYP/aug-cc-pVTZ level of theory.

	Energy (eV)	f_0	symmetry	Major assignment
1	6.513	0.010227	A	HOMO->LUMO (96%)
2	6.942	0.010956	A	HOMO->L+2 (92%)
3	6.975	0.022774	A	HOMO->L+1 (92%)
4	7.053	0.007146	A	HOMO->L+3 (82%)
5	7.349	0.006189	A	H-1->LUMO (98%)
6	7.702	0.006827	A	HOMO->L+4 (94%)
7	7.802	0.006559	A	H-1->L+2 (54%), HOMO->L+5 (11%), HOMO->L+6 (24%)
8	7.812	0.008853	A	H-1->L+2 (33%), HOMO->L+5 (18%), HOMO->L+6 (31%)
9	7.833	0.008355	A	H-1->L+1 (86%), H-1->L+2 (10%)
10	7.923	0.003004	A	HOMO->L+5 (63%), HOMO->L+6 (30%)
11	7.990	0.03192	A	H-1->L+3 (88%)
12	8.102	0.005151	A	HOMO->L+7 (72%)
13	8.555	0.006358	A	HOMO->L+8 (84%)
14	8.576	0.013288	A	H-1->L+4 (93%)
15	8.691	0.013091	A	H-1->L+5 (39%), H-1->L+6 (51%)
16	8.767	0.014571	A	HOMO->L+9 (64%), HOMO->L+10 (17%)
17	8.796	0.009869	A	H-1->L+5 (54%), H-1->L+6 (40%)
18	0.888	0.001955	A	HOMO->L+9 (25%), HOMO->L+10 (59%)
19	8.955	0.003897	A	HOMO->L+10 (16%), HOMO->L+13 (42%), HOMO->L+15 (14%)
20	9.052	0.012856	A	H-2->LUMO (93%)
21	9.104	0.00246	A	HOMO->L+11 (85%)
22	9.210	0.05082	A	H-1->L+7 (79%)
23	9.249	0.004712	A	HOMO->L+12 (72%), HOMO->L+14 (10%)
24	0.931	0.027542	A	H-3->LUMO (90%)
25	9.381	0.011222	A	HOMO->L+12 (15%), HOMO->L+14 (69%)
26	9.450	0.001418	A	H-1->L+8 (84%)
27	9.486	0.008782	A	HOMO->L+13 (26%), HOMO->L+15 (50%)
28	0.954	0.040072	A	H-2->L+1 (71%), H-2->L+2 (21%)
29	9.561	0.023613	A	H-2->L+1 (21%), H-2->L+2 (74%)
30	9.642	0.005202	A	H-1->L+9 (86%)
31	9.736	0.001148	A	H-2->L+3 (49%), H-1->L+10 (30%)
32	9.767	0.004133	A	H-2->L+3 (33%), H-1->L+10 (51%)
33	9.776	0.016136	A	H-3->L+1 (45%), H-3->L+2 (30%), HOMO->L+16 (19%)
34	9.779	0.032108	A	H-3->L+1 (22%), H-3->L+2 (62%)
35	9.815	0.007726	A	H-3->L+1 (23%), HOMO->L+15 (10%), HOMO->L+16 (58%)
36	9.936	0.008733	A	H-3->L+3 (26%), HOMO->L+17 (49%)
37	9.939	0.006957	A	H-3->L+3 (19%), H-1->L+11 (27%), HOMO->L+18 (26%)
38	9.954	0.00654	A	H-3->L+3 (13%), H-1->L+11 (52%), HOMO->L+18 (16%)
39	9.975	0.002324	A	H-3->L+3 (28%), HOMO->L+17 (31%), HOMO->L+18 (24%)
40	10.078	0.023117	A	H-4->LUMO (86%)

Table S4. Ground state frequencies (in cm^{-1}) of propylene oxide.

	CAMB3LYP/aug-cc-pVTZ	CAMB3LYP/aug-cc-pVQZ	B3LYP/aug-cc-pVTZ	Exp ref.[19]	Assignment
1	3194.1	3192.9	3162.7	3051	CH2 asym-stretch
2	3138.3	3137.6	3106.8	3001	CH stretch
3	3118.2	3117.6	3084.4	2995	CH3 asym-str
4	3117.8	3117.2	3083.2	2974	CH3 asym-str
5	3108.7	3107.5	3079.1		CH2 sym-stretch
6	3054.7	3053.6	3026.0	2942	CH3 sym-stretch
7	1549.4	1550.5	1531.6	1514	CH2 sciss
8	1504.6	1505.4	1496.6	1459	CH3 asym-deform
9	1491.3	1492.1	1485.1	1447	CH3 asym-deform
10	1458.3	1459.3	1436.4	1411	CH bending
11	1415.2	1416.4	1406.3	1371	CH3 umbrella
12	1309.6	1311.3	1291.6	1271	ring breathing
13	1203.9	1205.1	1188.5	1170	CH2 rock
14	1182.7	1183.8	1168.8	1147	CH bend
15	1175.8	1177.8	1158.5	1133	CH2 wag
16	1143.6	1145.4	1130.5	1108	CH2 twist
17	1054.1	1054.9	1043.3	1027	CH2. CH3 rock
18	997.8	998.7	969.8	954	ring deform
19	920.6	921.0	909.5	894	CH2. CH3 rock
20	872.3	873.2	841.9	834	ring CC stretching
21	798.6	799.5	768.9	756	CO asym str
22	413.2	414.2	408.6	409	CH3 bend
23	376.4	377.0	372.9	375	CH3 bend
24	211.3	211.7	212.4	200	CH3 torsion

Table S5. Ground state frequencies (in cm^{-1}) of propylene oxide cation.

	CAMB3LYP/aug-cc-pVTZ	CAMB3LYP/aug-cc-pVQZ	B3LYP/aug-cc-pVTZ	assignment
1	3169.0	3168.9	3140.9	CH stretch
2	3161.1	3160.9	3131.8	CH2 asym-stretch
3	3136.5	3136.5	3099.5	CH3 asym-str
4	3118.0	3116.1	3079.2	CH3 asym-str
5	3066.0	3064.5	3033.6	CH2 sym-stretch
6	3057.8	3056.9	3013.7	CH3 sym-stretch
7	1492.4	1493.0	1483.6	CH3 asym-deform
8	1465.1	1464.9	1436.4	CH3 asym-deform
9	1443.9	1444.6	1424.4	CH2 sciss
10	1412.8	1413.8	1393.7	CH3 umbrella
11	1379.1	1378.4	1343.9	
12	1263.0	1263.3	1243.6	
13	1191.0	1191.7	1171.6	CH bend
14	1170.2	1171.3	1149.1	CH2 wag
15	1122.8	1121.9	1101.3	CH2. CH3 rock
16	1035.2	1035.5	1017.6	CH2 twist
17	940.3	942.6	928.3	ring deform
18	922.4	924.7	908.4	CH2. CH3 rock
19	754.0	753.1	739.9	
20	713.5	703.8	630.1	ring CC stretching
21	436.5	441.9	398.0	CO asym str
22	344.9	347.6	335.4	CH3 bend
23	295.4	294.2	264.8	CH3 bend
24	186.4	187.8	172.4	CH3 torsion

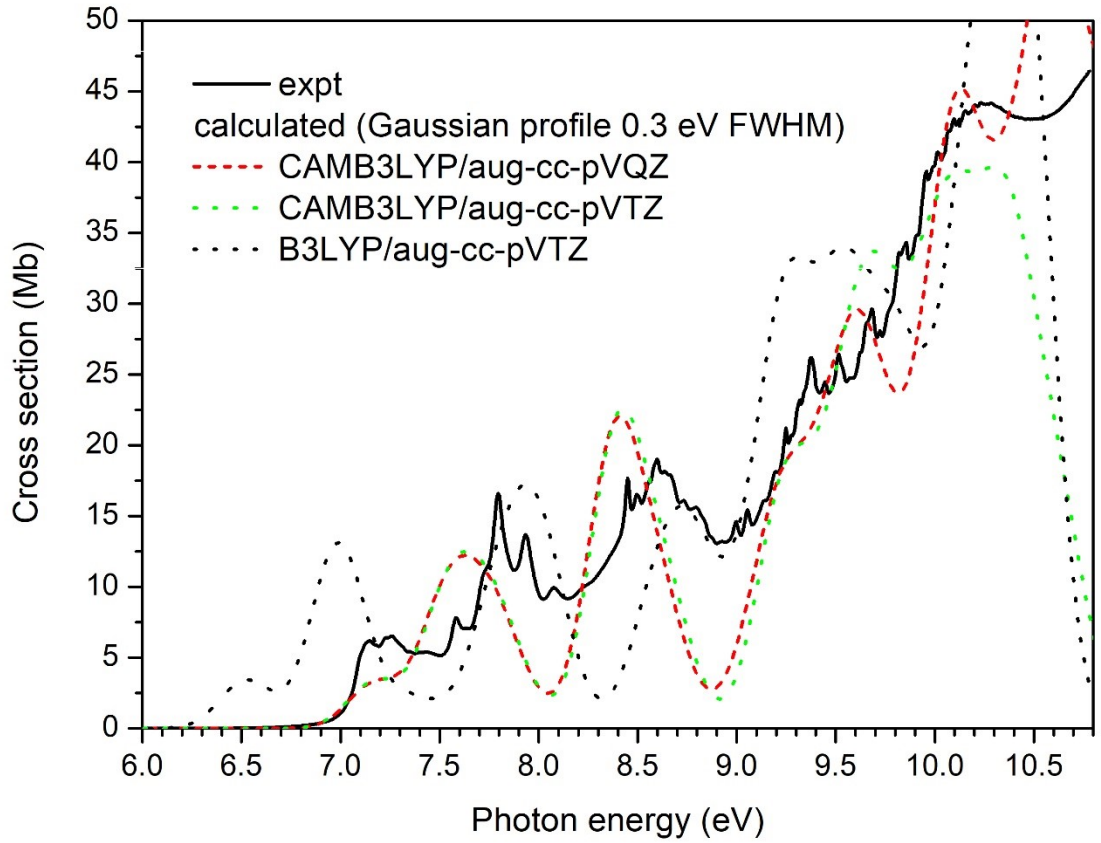


Figure S2. Comparison between the experimental (solid black) and calculated photoabsorption cross-section of propylene oxide, obtained in the vertical approximation, with a Gaussian profile, for different basis set and functionals: CAMB3LYP-aug-cc-pVQZ (red dashed), CAMB3LYP-aug-cc-pVTZ (dotted green) and B3LYP/aug-cc-pVTZ (dotted black).

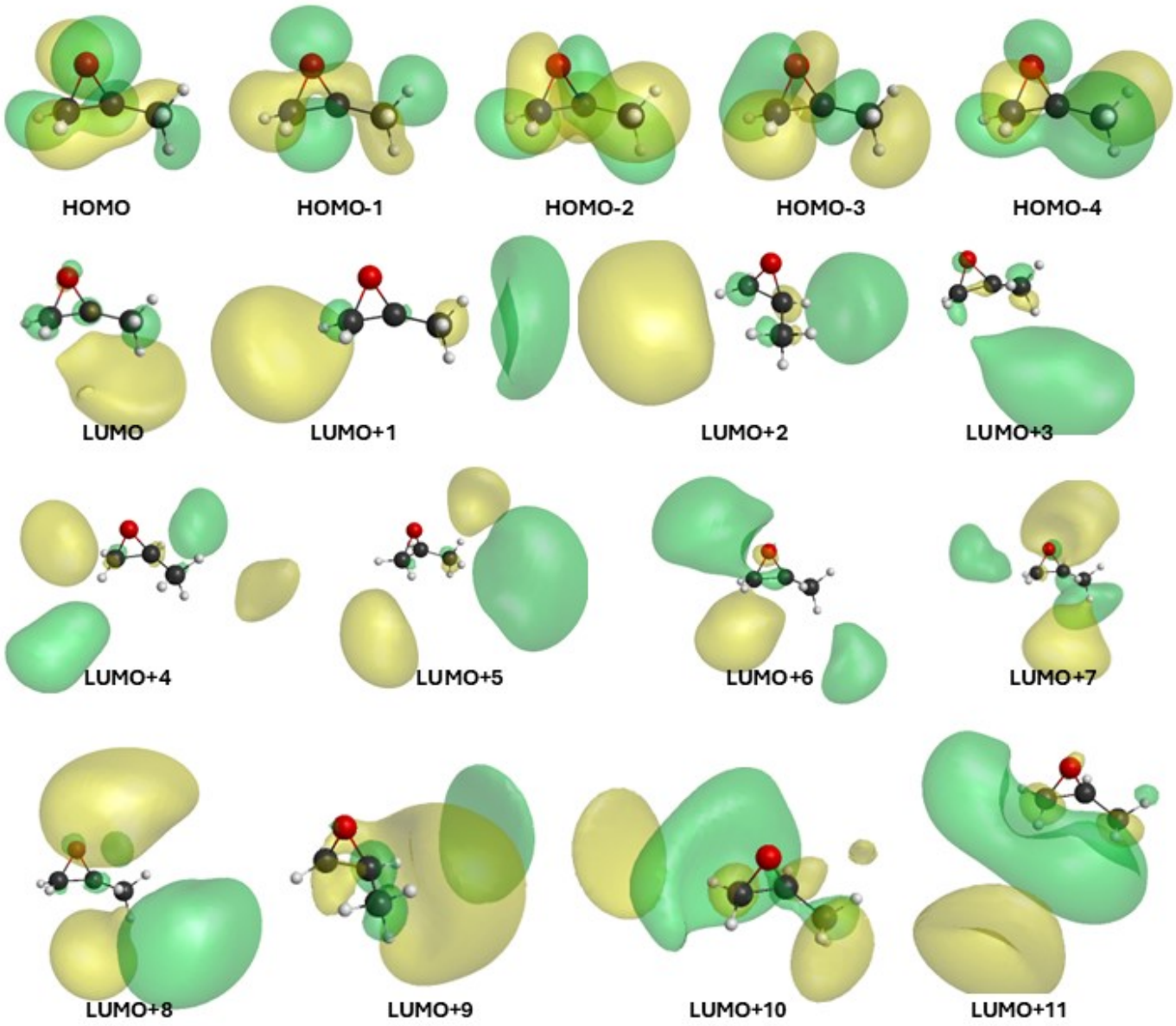
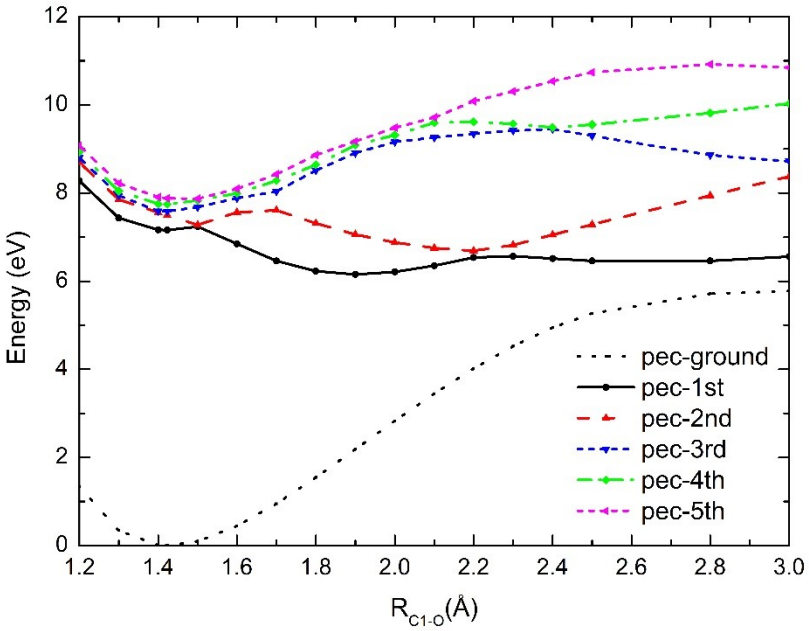


Figure S3. Most active molecular orbitals for propylene oxide, obtained at the TDDFT/CAMB3LYP/aug-cc-pVQZ level.

Figure S4. Potential energy curves of the five lowest singlet excited states of propylene oxide along each C–O stretching coordinate at the TDDFT/CAMB3LYP/aug-cc-pVTZ level. C2 denotes the carbon atom attached to the methyl group.

(a) C1-O stretching



(b) C2-O stretching