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Unimolecular Isomerizations and Oxygen Atom Loss in Formaldehyde and Acetaldehyde Carbonyl Oxides. A Theoretical Investigation

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Supporting Information

Cartesian coordinates (Bohr) of the CASSCF optimized structures:

SA1 CASSCF(8,8)/basis A

O	.0047803	-.0011283	.0000000
O	2.5620494	-.0053328	.0000000
C	3.6970177	2.1595590	.0000000
H	2.5954728	3.8536066	.0000000
H	5.7133851	2.0546993	.0000000

SA1 CASSCF(8,8)/basis B

O	-.0043578	.0016392	.0000000
O	2.5764463	-.0020030	.0000000
C	3.6911374	2.1515796	.0000000

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H	2.5807966	3.8470848	.0000000
H	5.7146175	2.0594612	.0000000

SA2 CASSCF(10,9)/basis A

C	.0000000	.0000000	.0000000
O	2.2072803	1.4564339	.0000000
O	2.2072803	-1.4564339	.0000000
H	-1.0833441	.0000000	-1.7273064
H	-1.0833441	.0000000	1.7273064

SA2 CASSCF(10,9)/basis B

C	.0000000	.0000000	.0000000
O	2.2092686	1.4547202	.0000000
O	2.2092686	-1.4547202	.0000000
H	-1.0791598	.0000000	-1.7354329
H	-1.0791598	.0000000	1.7354329

SATS1 CASSCF(8,8)/basis A

O	-.0011434	-.0073959	-.0431523
O	2.7711005	-.0011490	-.0101841
C	2.8884144	.0200723	2.4693042
H	4.1736760	-1.2757978	3.3660861
H	1.7717272	1.3356877	3.5170299

SATS1 CASSCF(8,8)/basis B

O	.0000000	.0000000	.0000000
O	2.7971737	.0000000	.0000000
C	2.8950203	2.4611877	.0000000

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H	1.7889013	3.5162828	-1.3284088
H	4.1926777	3.3563313	1.2978252

SATS2 CASSCF(8,8)/basis A

O	.0000000	.0000000	.0000000
O	2.5738068	.0000000	.0000000
C	3.4714085	2.5488783	.0000000
H	4.2635153	3.1400676	-1.7682963
H	4.2635153	3.1400676	1.7682963

SATS3 CASSCF(8,8)/basis A

O	.0000000	.0000000	.0000000
O	2.5775862	.0000000	.0000000
C	3.4516867	2.5530385	.0000000
H	3.2502872	3.5201363	-1.7686068
H	3.2502872	3.5201363	1.7686068

SATS4 CASSCF(8,8)/basis A

C	.0000000	.0000000	.0000000
O	.0000000	.0000000	2.2750088
H	1.7621043	.0000000	-1.0498189
H	-1.7621043	.0000000	-1.0498189
O	.0000000	.0000000	5.0972176

STAC CASSCF(8,8)/basis A

O	-2.0234118	.5547474	.0449284
O	.0005536	-1.0318476	-.0581744
C	2.2549178	.4158750	-.0226436
H	2.3879999	1.8910240	-1.4064746

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H	2.8672995	.7291483	1.8863111

TA1 CASSCF(8,8)/basis A

O	.0000000	.0000000	.0000000
O	2.6002630	.0000000	.0000000
C	3.3909609	2.5702040	.0000000
H	2.4242550	3.7566228	1.3272905
H	5.3991651	2.6738281	-.2453328

TA2 CASSCF(8,8)/basis A

O	.0002084	.0001826	.0000000
O	2.6208523	-.0007513	.0000000
C	3.4860203	2.5128311	.0000000
H	3.3299988	3.4925172	-1.7669956
H	3.3299988	3.4925172	1.7669956

TATS1 CASSCF(8,8)/basis A

O	.0035952	.0128113	.0000000
O	2.6121044	-.0191664	.0000000
C	3.5133743	2.4896557	.0000000
H	4.2414079	3.1351694	1.7751095
H	4.2414079	3.1351694	-1.7751095

TATS2 CASSCF(8,8)/basis A

O	.0000000	.0000000	.0000000
O	.0000000	.0000000	2.5965738
C	2.5613378	.0000000	3.4428260
H	3.9328732	.0000000	1.9584248

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H	2.7874836	-1.1349379	5.1068526

TATS3 CASSCF(8,8)/basis A

O	-.2975285	.0961510	.0000000
O	2.6113094	-.0851226	.0000000
C	3.5981897	2.2600210	.0000000
H	3.7499439	3.2428828	1.7691730
H	3.7499439	3.2428828	-1.7691730

SB1 CASSCF(8,8)/basis A

O	-.0260675	-.0956091	.0000000
O	2.5698048	-.0067890	.0000000
C	3.5810020	2.2017663	.0000000
H	5.6052343	2.1340082	.0000000
C	2.0287978	4.5295786	.0000000
H	3.2176140	6.1925208	.0000000
H	.8034803	4.5357438	1.6441203
H	.8034803	4.5357438	-1.6441203

SB2 CASSCF(8,8)/basis A

O	-.0460759	-.0578671	.0000000
O	2.5569799	.0382076	.0000000
C	3.5844663	2.2271459	.0000000
H	2.3392793	3.8264633	.0000000
C	6.3943234	2.3842911	.0000000
H	7.2148207	.5114576	.0000000
H	7.0529042	3.4009196	1.6553329
H	7.0529042	3.4009196	-1.6553329

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SB3 CASSCF(10,9)/basis A

C	-.3357548	.8873317	.0000000
O	1.5873244	-.2140570	-1.4563494
O	1.5873244	-.2140570	1.4563494
H	-.3315238	2.9294190	.0000000
C	-2.8830167	-.3576887	.0000000
H	-2.6586821	-2.3896258	.0000000
H	-3.944864	.2091399	-1.6605080
H	-3.9448640	.2091399	1.6605080

SB4 CASSCF(8,8)/basis A

C	-.0202990	-.0039275	-.0016565
O	2.6199107	.1727536	.0249312
H	-.7522726	1.8868751	-.0042035
O	3.6998990	-2.4024353	-.0695225
H	4.5276601	-2.3935592	1.5789137
C	-1.4455321	-2.0752686	-.0182591
H	-3.4630774	-1.8677919	-.0388656
H	-.6663985	-3.9413940	-.0402158

SBTS1 CASSCF(8,8)/basis A

O	-.0118772	-.1837968	-.0119761
O	2.8295683	.0287822	.0078988
C	2.7451306	2.4744556	.0236291
H	4.0134992	3.3555445	1.3663602
C	1.4072984	4.1315248	-1.8272194
H	.6408895	3.0177900	-3.3539614
H	2.7373944	5.5294267	-2.5358227

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H	-.1290030	5.1361084	-.9185832

SBTS2 CASSCF(8,8)/basis A

O	-.0089871	-.0537695	.0373149
O	2.8147060	.0596347	-.1044748
C	2.8558516	2.5032615	.0448072
H	1.5911917	3.5589554	-1.1302570
C	4.6755284	3.7500430	1.7911676
H	3.7378765	4.1256890	3.5805810
H	5.3247666	5.5345322	1.0264259
H	6.2658428	2.5145800	2.1582964

SBTS3 CASSCF(8,8)/basis A

O	-.1271239	.3204198	-.1733460
O	2.3829691	-.1783774	.1364341
C	3.7745152	2.1532433	.0670965
H	3.6644774	3.1781866	1.8151537
C	3.9096699	3.4459178	-2.4303828
H	4.5398121	2.1426651	-3.8807621
H	2.0715443	4.1781900	-2.9824661
H	5.2257110	5.0132410	-2.3391327

SBTS4 CASSCF(8,8)/basis A

O	.0488496	-.1386050	-.0386741
O	2.6141413	.0145082	.1066342
C	3.3706081	2.6237982	-.0177474
H	4.0655821	3.2827625	1.7727249
C	4.5716921	3.3732532	-2.4533077
H	3.2875808	3.0460424	-4.0162801

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H	5.0658830	5.3607690	-2.4139120
H	6.2846748	2.2917956	-2.8033115

SBTS5 CASSCF(8,8)/basis A

C	.0249989	-.0064662	.0200805
O	2.4827599	.1747186	-.0508950
H	-.8768634	1.8103526	.1260912
C	-1.0371483	-2.3959190	.3958709
H	-2.9402941	-2.4240738	1.1145420
H	-.6797975	-3.7921730	-1.0494901
H	1.3095970	-3.0275028	1.3536361
O	3.4934786	-2.3486593	.3477300

TB1 CASSCF(8,8)/basis A

O	.0521233	-.3750759	.2990644
O	2.4607802	.0306296	-.5856519
C	3.4091431	2.2846458	.5627660
H	5.4242468	2.1176250	.7344614
C	2.1883231	4.7093611	-.2018280
H	.1751694	4.6503964	.1649372
H	2.4659045	5.0807739	-2.2051190
H	3.0005082	6.2632287	.8574436

TB2 CASSCF(8,8)/basis A

O	.0005439	-.0144217	.1206544
O	2.5524445	-.0960368	-.3275093
C	3.5542875	2.3614662	.2186885
H	2.4174498	3.8592998	-.5466804

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C	6.3663119	2.3801853	.0434869
H	7.1743425	.9360772	1.2520260
H	7.0866787	4.2033147	.6361214
H	7.0063558	2.0316587	-1.8792075

TB3 CASSCF/(8,8)basis A

O	-.1583584	.3044037	-.1324870
O	2.4077373	-.1663655	.1028781
C	3.7376512	2.1538045	.0610570
H	3.5964090	3.1928389	1.7996532
C	3.9472534	3.4484966	-2.4325559
H	4.6145166	2.1458266	-3.8664780
H	2.1248689	4.1835243	-3.0335791
H	5.2598090	5.0162559	-2.3049216

TBTS1 CASSCF(8,8)/basis A

O	.0223630	-.1484865	.0560930
O	2.6178307	.0139295	.0230876
C	3.3324585	2.6045739	-.0621324
H	3.8441011	3.3373146	1.7603285
C	4.6361098	3.3935279	-2.4321006
H	3.4680080	2.9786357	-4.0639052
H	5.0132816	5.4065659	-2.3895249
H	6.4273696	2.4123603	-2.6697800

TBTS2 CASSCF(8,8)/basis A

O	0.0017813	-.2545390	-.0250975
O	2.5769586	-.0252405	.0313956
C	3.3163064	2.6035340	-.0410781

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H	5.0390846	2.7804970	1.0188428
C	1.3635545	4.6367425	.0376232
H	.0279491	4.4616978	-1.4999778
H	2.3182967	6.4420617	-.1311324
H	.3107802	4.6330012	1.8002903

TBTS3 CASSCF(8,8)/basis A

O	-.0356428	.0141454	-.2002296
O	2.5205490	-.0492971	.2207778
C	3.4865389	2.4883258	.1234571
H	2.0154785	3.8649474	-.0744008
C	5.9280049	2.6736884	-1.2746581
H	7.2893047	1.3257343	-.5470920
H	6.7079165	4.5560186	-1.0632455
H	5.6737907	2.3005924	-3.2803901

TBTS4 CASSCF(8,8)/basis A

O	-.0211820	.0208515	.0153499
O	-.0270754	-.0122832	2.9195347
C	2.3795912	.0016195	3.7770647
H	3.2620328	1.8272273	3.9347748
C	3.9014253	-2.3701812	3.6691597
H	2.7649139	-3.9785018	4.2343751
H	4.5801294	-2.7087988	1.7580822
H	5.5298367	-2.2365133	4.9058919

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Table 1. Total Energies (*E*, hartrees), Zero-Point Vibrational Energies (ZPVE, kcal/mol), and Dipole Moments (μ, debyes) for CASSCF/Basis A Optimized Structures of the Stationary Points on the Singlet and Triplet CH_2O_2 Potential Energy Surfaces

				E						
structure	point group	state	n.i.f.[a]	CASSCF/ basis A	MRDCI/ basis A	MRDCI+Q/ basis A	MRDCI/ basis B	MRDCI+Q/ basis B	ZPVE[b]	μ[c]
				singlet potential energy surface						
SA1	C_s	$^1A'$	0	-188.71115	-189.03005	-189.06612	-189.13538	-189.17330	18.0	3.86
SA2	C_{2v}	$^1A_1$	0	-188.76416	-189.08341	-189.11565	-189.18350	-189.22092	19.4	2.71
SATS1	C_1	^1A	1	-188.67992	-188.98885	-189.02494	-189.09366	-189.13365	17.1	3.27
SATS2	C_s	$^1A'$	1	-118.66765	-188.98573	-189.01995	-189.08912	-189.12944	16.5	2.41
SATS3	C_s	$^1A'$	1	-118.66818	-188.98556	-189.02024	-189.08985	-189.13019	16.6	2.23
SATS4	C_{2v}	$^1A'$	2	-118.63683	-188.97010	-189.00160	-189.07409	-189.11308		4.68
				triplet potential energy surface						
TA1	C_1	^3A	0	-188.67286	-188.99057	-189.02073	-189.09312	-189.12388	16.7	2.09
TA2	C_s	$^3A''$	0	-188.67277	-188.99425	-189.02371	-189.10020	-189.13273	16.6	2.17

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Table 1. (Continuation)

TATS1	C_s	^{3}A''	1	-188.67080	-188.98918	-189.02078	-189.09450	-189.12987	16.2	2.32
TATS2	C_1	^{3}A	1	-188.67189	-188.98731	-189.01911	-189.09389	-189.12917	16.7	2.03
TATS3	C_s	^{3}A''	1	-188.66900	-188.98515	-189.01746	-189.09180	-189.12524	15.6	2.15

[a]Number of imaginary vibrational frequencies.

[b]Calculated using CASSCF/basis A vibrational frequencies scaled by 0.8929.

[c]Calculated at the CASSCF/basis A level.

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Table 2. Total Energies (E, hartrees), Zero-Point Vibrational Energies (ZPVE, kcal/mol), and Dipole Moments (μ, debyes) for CASSCF/Basis A Optimized Structures of the Stationary Points on the Singlet and Triplet $C_2H_4O_2$ Potential Energy Surfaces

				E				
structure	point group	state	n.i.f.[a]	CASSCF/ basis A	MRDCI/ basis A	MRDCI+Q/ basis A	ZPVE[b]	μ[c]
				singlet potential energy surface				
SB1	C_s	$^1A'$	0	-227.76093	-228.19359	-228.23790	35.2	4.31
SB2	C_s	$^1A'$	0	-227.75680	-228.18773	-228.23389	34.9	4.94
SB3	C_s	$^1A'$	0	-227.81168	-228.24051	-228.28426	36.1	2.89
SB4	C_1	^1A	0	-227.77013	-228.22097	-228.26874	34.4	1.65
SBTS1	C_1	^1A	1	-227.72356	-228.14444	-228.19135	34.4	3.96
SBTS2	C_1	^1A	1	-227.72949	-228.15247	-228.19967	34.1	4.42
SBTS3	C_1	^1A	1	-227.71330	-228.13633	-228.18328	33.9	2.40
SBTS4	C_1	^1A	1	-227.71248	-228.13931	-228.18702	33.8	2.61

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Table 2. (Continuation)

SBTS5	C_1	^1A	1	-227.70600	-228.15304	-228.20284	34.4	3.96
				triplet potential energy surface				
TB1	C_1	^3A	0	-227.71665	-228.14674	-228.19038	34.3	2.37
TB2	C_1	^3A	0	-227.71700	-228.14395	-228.18553	34.3	2.37
TB3	C_1	^3A	0	-227.71777	-228.14918	-228.19034	34.3	2.35
TBTS1	C_1	^3A	1	-227.71508	-228.14146	-228.18429	33.8	2.53
TBTS2	C_1	^3A	1	-227.71245	-228.13641	-228.17896	34.2	2.26
TBTS3	C_1	^3A	1	-227.71592	-228.13997	-228.18476	34.1	2.31
TBTS4	C_1	^3A	1	-227.71415	-228.14406	-228.18740	32.9	2.34

[a]Number of imaginary vibrational frequencies.

[b]Calculated using CASSCF/basis A vibrational frequencies, scaled by 0.8929.

[c]Calculated at the CASSCF/basis A level.

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Table 3. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **SA1** Calculated at the CASSCF(8,8)/basis A Level

mode	sym	approx assgnmnt	frequencies		IR int
			unscaled	scaled	
ν_1	a'	asym CH stretch	3537	3158	0.2
ν_2	a'	sym CH stretch	3379	3017	16.6
ν_3	a'	CH_2 scissor	1596	1425	19.3
ν_4	a'	CH_2 rock + CO stretch	1305	1165	10.5
ν_5	a'	CO stretch + CH_2 rock	1238	1105	244.4
ν_6	a'	OO stretch	955	853	160.1
ν_7	a''	CH_2 wag	843	753	37.3
ν_8	a''	CH_2 twist	711	635	9.6
ν_9	a'	OOC deform.	548	489	0.6

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Table 4. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **SA2** Calculated at the CASSCF(10,9)/basis A Level

mode	sym	approx assgnmnt	frequencies		IR int
			unscaled	scaled	
ν_1	b_1	asym CH stretch	3362	3002	58.8
ν_2	a_1	sym CH stretch	3321	2965	20.3
ν_3	a_1	CH_2 scissor	1689	1508	7.3
ν_4	b_2	CH_2 wag	1395	1246	1.1
ν_5	b_1	CH_2 rock	1304	1164	9.3
ν_6	a_1	sym CO stretch	1296	1157	42.2
ν_7	a_2	CH_2 twist	1119	999	0.0
ν_8	b_2	asym CO stretch	934	834	18.3
ν_9	a_1	OOC deform. + OO deform.	754	673	2.4

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Table 5. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **TA1** Calculated at the CASSCF(8,8)/basis A Level

mode	approx assgnmnt	frequencies		IR int
		unscaled	scaled	
ν_1	asym CH stretch	3483	3109	9.9
ν_2	sym CH stretch	3338	2981	11.7
ν_3	CH_2 scissor	1560	1393	5.8
ν_4	CH_2 rock	1251	1117	11.2
ν_5	CO stretch	1083	967	89.6
ν_6	OO stretch	979	874	3.9
ν_7	CH_2 wag	918	820	20.0
ν_8	OOC deform.	504	450	1.9
ν_9	CH_2 twist	199	178	6.6

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Table 6. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **TA2** Calculated at the CASSCF(8,8)/basis A Level

mode	sym	approx assgnmnt	frequencies		IR int
			unscaled	scaled	
ν_1	a''	asym CH stretch	3473	3101	17.7
ν_2	a'	sym CH stretch	3336	2979	15.5
ν_3	a'	CH_2 scissor	1589	1419	16.5
ν_4	a''	CH_2 rock	1207	1078	7.3
ν_5	a'	CO stretch	1083	967	37.4
ν_6	a'	OO stretch	891	796	28.0
ν_7	a'	CH_2 wag	826	738	6.8
ν_8	a'	OOC deform.	455	406	7.3
ν_9	a''	CH_2 twist	168	150	0.0

Table 7. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **SB1** and **SB2** Calculated at the CASSCF(8,8)/basis A Level

			SB1			SB2		
			frequencies			frequencies		
mode	sym	approx assgnmnt	unscaled	scaled	IR int	unscaled	scaled	IR int
ν_1	a'	CH stretch	3424	3057	9.5	3421	3055	11.4
ν_2	a'	asym CH_3 stretch	3318	2963	14.1	3316	2961	6.9
ν_3	a''	asym CH_3 stretch	3278	2927	5.1	3268	2918	14.0
ν_4	a'	sym CH_3 stretch	3224	2879	9.4	3213	2869	16.9
ν_5	a'	CH_2 scissor	1614	1441	16.3	1636	1461	22.2
ν_6	a''	CCH bend	1604	1432	7.8	1613	1440	9.9
ν_7	a'	CCH bend + CC stretch	1603	1431	41.7	1581	1412	5.4
ν_8	a'	CH_3 umbrella +CCH bend	1539	1374	2.1	1544	1379	17.7
ν_9	a'	CO stretch	1339	1196	86.6	1351	1206	101.3
ν_{10}	a'	CH_3 umbrella	1218	1088	10.2	1238	1105	14.2

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Table 7. (Continuation)

ν_{11}	a''	CH_3 rock	1125	1005	0.0	1138	1016	0.1
ν_{12}	a'	CO stretch + CC stretch	1014	905	21.4	984	879	65.2
ν_{13}	a'	OO stretch	886	791	181.3	872	779	309.9
ν_{14}	a''	OCH bend + COO bend	730	652	17.4	868	775	14.9
ν_{15}	a'	OOC deform. + OCC deform.	687	613	8.5	564	504	10.3
ν_{16}	a''	CH_3 bend + COO bend	442	395	0.0	247	221	0.5
ν_{17}	a'	OOC deform. + OCC deform.	311	278	8.1	333	297	19.6
ν_{18}	a''	CH_3 torsion	208	186	2.1	142	127	1.5

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Table 8. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **SB3** Calculated at the CASSCF(10,9)/basis A Level

mode	sym	approx assgnmnt	frequencies		IR int
			unscaled	scaled	
ν_1	a'	CH stretch	3303	2949	49.1
ν_2	a'	sym CH_3 stretch	3321	2965	20.4
ν_3	a''	asym CH_3 stretch	3280	2929	23.5
ν_4	a'	sym CH_3 stretch	3223	2878	10.0
ν_5	a''	CH_3 bend	1629	1455	7.6
ν_6	a'	CH_2 scissor	1627	1453	5.7
ν_7	a'	CCH bend	1593	1422	42.5
ν_8	a'	CH_3 umbrella	1546	1380	4.0
ν_9	a'	sym CO stretch	1336	1193	41.3
ν_{10}	a''	OCH bend	1329	1187	0.6
ν_{11}	a'	CCH bend + CC stretch	1222	1091	15.1
ν_{12}	a''	OCH bend	1119	999	3.6
ν_{13}	a'	CC stretch	980	875	2.3
ν_{14}	a''	asym CO stretch	900	804	12.1
ν_{15}	a'	OOC bend	740	661	2.2
ν_{16}	a'	OO stretch	482	430	14.8
ν_{17}	a''	OOC deform.	396	354	0.3
ν_{18}	a''	CH_3 torsion	208	186	0.3

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Table 9. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **SB4** Calculated at the CASSCF(8,8)/basis A Level

mode	approx assgnmnt	frequencies		IR int
		unscaled	scaled	
ν_1	OH stretch	3682	3288	21.2
ν_2	asym CH_2 stretch	3467	3096	4.8
ν_3	CH stretch	3412	3046	9.8
ν_4	sym CH_2 stretch	3366	3006	2.9
ν_5	CC stretch	1798	1605	52.4
ν_6	CH_2 scissor + HCO scissor	1560	1393	9.6
ν_7	HCO bend + OOH bend	1424	1271	19.9
ν_8	OOH bend	1412	1261	39.4
ν_9	CCH bend + CO stretch	1210	1080	32.3
ν_{10}	CCH bend + OCH bend	995	888	27.3
ν_{11}	CO stretch	971	867	29.3
ν_{12}	CH_2 wag	831	742	46.9
ν_{13}	OO stretch	805	719	12.0
ν_{14}	HCCH twist	667	596	0.7
ν_{15}	OOC bend + OCC bend	619	553	6.4
ν_{16}	OOC bend + OCC bend	335	299	1.2
ν_{17}	OOH bend	195	174	125.4
ν_{18}	OOC bend	172	154	11.4

Table 10. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of **TB1**, **TB2** and **TB3** Calculated at the CASSCF(8,8)/basis A Level

		TB1			**TB2**			**TB3**		
		frequencies			frequencies			frequencies		
mode	approx assgnmnt	unscaled	scaled	IR int	unscaled	scaled	IR int	unscaled	scaled	IR int
ν_1	CH stretch	3365	3005	24.4	3376	3014	19.4	3377	3015	29.5
ν_2	asym CH_3 stretch	3311	2956	17.0	3293	2940	18.6	3292	2939	20.5
ν_3	asym CH_3 stretch	3268	2918	25.2	3262	2913	21.3	3267	2917	21.2
ν_4	sym CH_3 stretch	3209	2865	16.9	3199	2856	17.7	3207	2864	11.6
ν_5	CH_2 scissor	1633	1458	3.2	1632	1457	3.2	1630	1455	2.8
ν_6	CH_2 scissor	1623	1449	6.4	1618	1445	6.6	1619	1446	7.9
ν_7	CH_3 umbrella	1570	1402	11.0	1571	1403	12.5	1568	1400	9.9
ν_8	CCH bend	1475	1317	18.4	1446	1291	33.3	1463	1306	26.4
ν_9	CC stretch + CH3 bend	1219	1088	11.4	1240	1107	11.7	1215	1085	7.4
ν_{10}	CO stretch + CC stretch	1163	1038	23.8	1176	1050	25.7	1181	1055	23.4

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Table 10. (Continuaton)

ν_{11}	CC stretch + CH_3 bend	1143	1021	26.9	1148	1025	12.7	1139	1017	2.5
ν_{12}	OO stretch	989	883	23.6	1041	930	53.0	923	824	10.4
ν_{13}	CO stretch + CC stretch	915	817	13.2	935	835	12.8	882	788	24.6
ν_{14}	OCH bend + COO bend	705	629	13.4	773	690	12.4	703	628	9.4
ν_{15}	OOC deform.	534	477	1.7	513	458	5.9	521	465	5.3
ν_{16}	CCO deform.	371	331	4.4	319	285	0.4	377	337	5.3
ν_{17}	CH_3 torsion	219	196	0.6	199	178	0.7	189	169	2.5
ν_{18}	CH_3 bend + OOC bend	162	145	1.5	93	83	0.2	131	117	0.1

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Table 11. MRDCI+Q Calculated Vertical Excitation Energies (eV) for Formaldehyde and Acetaldehyde Carbonyl Oxides [a]

		H_2COO		$CH_3(H)COO$	
state	transition	basis A	basis B	syn	anti
$1^3A'$	$\pi_{OO}\rightarrow\pi^*_{CO}$	1.65	1.64	2.00	1.95
$1^3A''$	$\pi_{O1}\rightarrow\pi^*_{CO}$	2.05	2.09	2.41	2.36
$1^1A''$	$n_{O1}\rightarrow\pi^*_{CO}$	2.13	2.14	2.42	2.31
$2^1A'$	$\pi_{OO}\rightarrow\pi^*_{CO}$	3.60	3.96	4.83	4.39
$2^3A''$	$\sigma_{OO}\rightarrow\pi^*_{CO}$	6.33	6.38	6.22	6.24
$2^1A''$	$\sigma_{OO}\rightarrow\pi^*_{CO}$	6.88	6.80	6.37	6.48
$2^3A'$	$\pi_{CO}\rightarrow\pi^*_{CO}$	7.63	7.19	7.60	8.10

[a]At the CASSCF/basis A optimized equilibrium geometries.