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Supporting Information

Origin of ^{17}O NMR Chemical Shifts Based on Molecular Orbital Theory: Paramagnetic Terms of the Pre-α, α and β Effects from Orbital-to-Orbital Transitions, Along with the Effects from Vinyl, Carbonyl and Carboxyl Groups

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Table S1. The $\sigma^d(O)$, $\sigma^p(O)$, $\sigma^t(O)$ and $-\Delta\sigma^t_{Me_2O}(O)$ values (ppm) for some oxygen monomeric and dimeric species, together with observed values.[a]

Species (sym[b])	$\sigma^d(O)$	$\sigma^p(O)$	$\sigma^t(O)$	$-\Delta\sigma^t_{Me_2O}(O)$[c]	$\delta(O)$[d]
I (monomeric ethers)					
Me_2O (C_{2v})	396.12	–73.37	322.75	–52.5	–52.5
EtOMe (C_s)	397.46	–105.43	292.04	–21.8	–22.5
n-PrOMe (C_s)	400.83	–105.99	294.84	–24.6	–28.5
i-PrOMe (C_1)	401.79	–128.26	273.53	–3.3	–2.0
n-BuOMe (C_s)	405.13	–110.00	295.13	–24.9	–28.5
i-BuOMe (C_1)	399.41	–103.96	295.45	–25.2	–30.0
s-BuOMe (C_1)	401.88	–122.27	279.61	–9.4	–8.5
t-BuOMe (C_s)	405.31	–141.91	263.41	6.8	8.5
n-PeOMe (C_s)	407.52	–112.08	295.44	–25.2	–27.5
neo-PeOMe (C_s)	399.01	–100.22	298.78	–28.5	–32.5
s-PeOMe (C_1)	402.01	–123.86	278.15	–7.9	–16.5
i-PeOMe (C_1)	407.07	–110.46	296.61	–26.4	–29.5
neo-HexOMe (C_s)	408.35	–109.40	298.95	–28.7	–29.5
Et_2O (C_{2v})	396.85	–136.13	260.72	9.5	6.5
n-PrOEt (C_s)	398.61	–136.04	262.57	7.7	1.7
i-PrOEt (C_1)	398.34	–157.34	241.00	29.3	28.0
n-BuOEt (C_s)	403.02	–139.28	263.73	6.5	–1.5
i-BuOEt (C_1)	396.27	–132.29	263.97	6.3	–1.0
s-BuOEt (C_1)	396.89	–149.87	247.02	23.2	24.5
t-BuOEt (C_1)	397.91	–168.13	229.78	40.5	40.5
n-PeOEt (C_s)	404.45	–141.33	263.12	7.1	1.5
neo-PeOEt (C_s)	396.15	–128.31	267.84	2.4	–3.5
s-PeOEt (C_1)	396.73	–150.82	245.91	24.3	15.0
n-Pr_2O (C_{2v})	397.47	–132.00	265.47	4.8	–3.5
n-PrO*i*-Pr (C_1)	396.97	–153.65	243.32	26.9	24.0
i-Pr_2O (C_2)	401.23	–177.41	223.82	46.4	52.5
i-PrO*t*-Bu (C_1)	393.43	–184.19	209.25	61.0	62.5
n-Bu_2O (C_{2v})	407.04	–140.02	267.02	3.2	–7.0[e]
s-Bu_2O (C_2)	402.38	–167.35	235.03	35.2	41.5
t-Bu_2O (C_2)	393.82	–196.90	196.92	73.3	76.0
i-Pe_2O (C_2)	412.53	–143.08	269.45	0.8	–7.0[e]

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O: S) - \sigma^t(O: Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C.

(**Table S1** continued)

Species (sym[b])	σ^d(O)	σ^p(O)	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
(Me_2O (C_{2v})	396.12	–73.37	322.75	–52.5	–52.5)
II (monomeric alcohols)					
MeOH (C_s)	395.07	–72.87	322.20	–52.0	–37
EtOH (C_s)	398.40	–108.33	290.07	–19.8	6
n-PrOH (C_s)	401.99	–110.17	291.82	–21.6	0
i-PrOH (C_1)	402.81	–152.24	250.57	19.7	38
n-BuOH (C_s)	405.29	–112.68	292.62	–22.4	–4
i-BuOH (C_1)	401.13	–108.32	292.81	–22.6	–2
s-BuOH (C_1)	403.73	–147.36	256.37	13.9	34
t-BuOH (C_s)	406.99	–180.47	226.52	43.7	70
n-PeOH (C_s)	407.68	–115.32	292.37	–22.1	–7
III (monomeric carboxylic acids)					
HC(=O)OH (C_s)			6.58[f]	263.7	253[g]
=O	404.48	–506.77	–102.29	372.5	
–OH	399.82	–284.37	115.44	154.8	
MeC(=O)OH (C_s)			5.85[f]	264.4	251[g]
=O	401.79	–506.86	–105.07	375.3	
–OH	404.53	–287.76	116.77	153.5	
EtC(=O)OH (C_s)			13.74[f]	256.5	244[g]
=O	405.78	–498.53	–92.75	363.0	
–OH	408.25	–288.01	120.24	150.0	
i-PrC(=O)OH (C_1)			17.75[f]	252.5	242[g]
=O	404.40	–487.71	–83.31	353.6	
–OH	405.68	–286.88	118.80	151.4	
t-BuC(=O)OH (C_s)			16.47[f]	253.8	240[g,h]
=O	401.51	–491.71	–90.20	360.5	
–OH	401.99	–278.85	123.15	147.1	

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 ℃, pure liquids. [e]Measured at 100 ℃. [f]σ^t(O) was given as the average value of the oxygen at the carbonyl and hydroxy groups. [g]Due to rapid proton exchange, only one peak appeared. [h]Measured at 40 ℃.

(**Table S1** continued)

Species (sym[b])		σ^d(O)	σ^p(O)	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
cf:						
Me_2O (C_1)				561.36	–51.1	–52.5
	Unit 1	391.82	–69.25	322.57		
	Unit 2	399.57	–79.53	320.04		
IV (dimeric alcohols)						
MeOH (C_1)				316.36	–46.1	–37
	Acceptor	401.22	–84.86	316.36		
	Donor	400.39	–72.67	327.71		
EtOH (C_1)				285.04	–15.9	6
	Acceptor	397.63	–112.59	285.04		
	Donor	399.65	–112.49	287.16		
n-PrOH (C_1)				288.07	–17.8	0
	Acceptor	394.37	–107.80	286.58		
	Donor	402.41	–112.84	289.57		
i-PrOH (C_1)				248.46	21.8	38
	Acceptor	398.94	–153.99	244.95		
	Donor	407.38	–155.41	251.97		
n-BuOH (C_1)				288.90	–18.7	–4
	Acceptor	396.91	–109.81	287.09		
	Donor	408.91	–118.21	290.70		
i-BuOH (C_1)				289.84	–19.6	–2
	Acceptor	397.14	–109.57	287.57		
	Donor	405.98	–113.87	292.10		
s-BuOH (C_1)				253.49	16.8	34
	Acceptor	397.80	–151.06	246.74		
	Donor	411.83	–151.60	260.24		
t-BuOH (C_1)				223.95	46.3	70
	Acceptor	403.57	–184.56	219.01		
	Donor	412.42	–183.52	228.90		
n-PeOH (C_1)				288.76	–18.5	–7
	Acceptor	394.52	–107.32	287.20		
	Donor	410.79	–120.47	290.32		

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids.

(**Table S1** continued)

Species (sym[b])	σ^{d}(O)	σ^{p}(O)	σ^{t}(O)	$-\Delta\sigma^{t}_{Me_2O}$(O)[c]	δ(O)[d]
V (dimeric carboxylic acids)					
HC(=O)OH (C_s)			18.81[f]	251.4	253[g]
Acceptor	413.49	–468.43	–54.93		
Donor	405.29	–312.74	92.55		
MeC(=O)OH (C_{2h})			20.76[f]	249.5	251[g]
Acceptor	414.38	–470.91	–56.52		
Donor	417.39	–319.35	98.04		
EtC(=O)OH (C_{2h})			27.81[f]	242.4	244[g]
Acceptor	421.20	–467.63	–46.43		
Donor	423.29	–321.25	102.04		
i-PrC(=O)OH (C_i)[i]			32.39[f]	237.9	242[g]
Acceptor	424.31	–459.00	–34.70		
Donor	424.42	–324.94	99.48		
t-BuC(=O)OH (C_{2h})[i]			31.61[f]	238.6	240[g,h]
Acceptor	441.46	–484.83	–43.37		
Donor	427.41	–320.83	106.58		

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^{t}_{Me_2O}(O) = -[\sigma^{t}(O: S) - \sigma^{t}(O: Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C. [f]σ^{t}(O) was given as the average value of the oxygen at the carbonyl and hydroxy groups. [g]Due to rapid proton exchange, only one peak appeared. [h]Measured at 40 °C. [i]The optimization was conducted with tight convergence criteria and an ultrafine grid.

Table S2. The $\sigma^d(O)$, $\sigma^p(O)$, $\sigma^t(O)$ and $\Delta\sigma^t(O)$ values for some oxygen species calculated with CAM-B3LYP/BSS-A, together with the pre-α, α, β, γ and δ effects, corresponding to the $\Delta\sigma^t(O)$ values.

Species (sym)[a]	$\sigma^d(O)$	$\sigma^p(O)$	$\sigma^t(O)$	$-\Delta\sigma^t(O)$[b]	effect
O^{2-} (**1**: O_h)	408.45	0.00	408.45	0.00	---
OH^- (**2**: $C_{\infty v}$)	396.45	–18.14	378.31	30.13	pre-α
MeO^- (**3**: C_{3v})	411.68	–106.63	305.04	103.40	α
EtO^- (**4**: C_s)	416.27	–224.19	192.08	216.36	β
i-PrO^- (**5**: C_s)	419.24	–243.99	175.26	233.19	β
t-BuO^- (**6**: C_s)	424.00	–210.50	213.51	194.94	β
H_2O (**7**: C_{2v})	392.55	–61.89	330.65	77.79	pre-α
MeOH (**8**: C_s)	394.27	–63.05	331.22	77.23	α
EtOH (**9**: C_s)	397.56	–98.64	298.92	109.52	β
i-PrOH (**10**: C_1)	402.33	–142.72	259.61	148.84	β
t-BuOH (**11**: C_s)	406.26	–171.01	235.25	173.20	β
n-PrOH (**12**: C_s)	400.93	–100.30	300.63	107.82	γ
n-BuOH (**13**: C_s)	404.65	–103.23	301.43	107.02	δ
Me_2O (**14**: C_{2v})	394.65	–59.06	335.59	72.85	α
EtOMe (**15**: C_s)	396.04	–90.97	305.07	103.37	β
i-PrOMe (**16**: C_1)	400.60	–113.64	286.97	121.48	β
t-BuOMe (**17**: C_s)	404.04	–126.34	277.69	130.76	β
n-PrOMe (**18**: C_s)	399.20	–91.68	307.52	100.93	γ
n-BuOMe (**19**: C_s)	403.67	–95.65	308.01	100.43	δ
Et_2O (**20**: C_{2v})	395.35	–121.80	273.55	134.90	β
i-Pr_2O (**21**: C_2)	400.01	–161.78	238.23	170.22	β
t-Bu_2O (**22**: C_2)	389.44	–176.28	213.16	195.29	β
n-Pr_2O (**23**: C_{2v})	395.52	–117.52	278.00	130.45	γ
n-Bu_2O (**24**: C_{2v})	404.46	–124.90	279.56	128.89	δ
H_3O^+ (**25**: C_{3v})	396.83	–88.61	308.22	100.22	pre-α
MeH_2O^+ (**26**: C_s)	399.72	–86.66	313.06	95.39	α
EtH_2O^+ (**27**: C_1)	407.22	–124.08	283.14	125.31	β
Me_3O^+ (**28**: C_{3v})	402.36	–88.53	313.83	94.62	α
Et_3O^+ (**29**: C_3)	396.58	–138.59	257.99	150.46	β
OH^+ (**30**: $C_{\infty v}$)	386.76	630.34	1017.10	–608.65	pre-α
H_2C=CHOH (**31**: C_s)	402.08	–181.24	220.84	187.61	C=C
H_2C=CHOMe (**32**: C_s)	401.13	–156.58	244.55	163.90	C=C
PhOH (**33**: C_s)	392.00	–172.35	219.65	188.80	C_6H_5
H_2C=O (**34**: C_{2v})	403.91	–837.06	–433.14	841.59	C=O
HC(=O*)OH (**35**: C_s)	404.14	–500.88	–96.74	505.19	OC=O
HC(=O)O*H (**36**: C_s)	399.28	–273.62	125.66	282.79	OC=O

[a]Symmetry. [b]$-\Delta\sigma^t(O) = -[\sigma^t(O: S) - \sigma^t(O: O^{2-})]$.

Table S3. The $\sigma^{d}(O)$, $\sigma^{p}(O)$, $\sigma^{t}(O)$ and $\Delta\sigma^{t}(O)$ values for some oxygen species calculated with PBE/BSS-A, together with the pre-α, α, β, γ and δ effects, corresponding to the $\Delta\sigma^{t}(O)$ values.

Species (sym)[a]	$\sigma^{d}(O)$	$\sigma^{p}(O)$	$\sigma^{t}(O)$	$-\Delta\sigma^{t}(O)$[b]	effect
O^{2-} (**1**: O_h)	407.92	0.00	407.92	0.00	---
OH^- (**2**: $C_{\infty v}$)	395.70	–12.85	382.85	25.07	pre-α
MeO^- (**3**: C_{3v})	419.25	–162.45	256.80	151.12	α
EtO^- (**4**: C_s)	422.66	–377.84	44.82	363.11	β
i-PrO^- (**5**: C_s)	427.93	–357.88	70.04	337.88	β
t-BuO^- (**6**: C_s)	431.69	–233.01	198.67	209.25	β
H_2O (**7**: C_{2v})	392.11	–68.49	323.62	84.30	pre-α
MeOH (**8**: C_s)	395.04	–79.55	315.48	92.44	α
EtOH (**9**: C_s)	398.36	–116.65	281.71	126.22	β
i-PrOH (**10**: C_1)	402.71	–163.60	239.11	168.81	β
t-BuOH (**11**: C_s)	407.90	–192.64	215.26	192.66	β
n-PrOH (**12**: C_s)	402.03	–118.47	283.56	124.36	γ
n-BuOH (**13**: C_s)	404.85	–120.41	284.44	123.49	δ
Me_2O (**14**: C_{2v})	396.70	–84.50	312.21	95.72	α
EtOMe (**15**: C_s)	398.01	–117.75	280.26	127.66	β
i-PrOMe (**16**: C_1)	403.30	–142.81	260.49	147.43	β
t-BuOMe (**17**: C_s)	408.28	–157.83	250.44	157.48	β
n-PrOMe (**18**: C_s)	401.33	–118.00	283.32	124.60	γ
n-BuOMe (**19**: C_s)	405.22	–121.67	283.55	124.38	δ
Et_2O (**20**: C_{2v})	397.46	–149.80	247.66	160.27	β
i-Pr_2O (**21**: C_2)	407.01	–199.02	207.99	199.93	β
t-Bu_2O (**22**: C_2)	404.24	–222.79	181.45	226.48	β
n-Pr_2O (**23**: C_{2v})	397.69	–144.82	252.87	155.06	γ
n-Bu_2O (**24**: C_{2v})	406.41	–151.82	254.58	153.34	δ
H_3O^+ (**25**: C_{3v})	396.14	–95.55	300.59	107.33	pre-α
MeH_2O^+ (**26**: C_s)	399.60	–102.06	297.54	110.39	α
EtH_2O^+ (**27**: C_1)	407.94	–142.86	265.08	142.84	β
Me_3O^+ (**28**: C_{3v})	401.72	–122.33	279.38	128.54	α
Et_3O^+ (**29**: C_3)	398.67	–183.22	215.45	192.47	β
OH^+ (**30**: $C_{\infty v}$)	—	—	—	—	pre-α
H_2C=CHOH (**31**: C_s)	402.99	–208.66	194.32	213.60	C=C
H_2C=CHOMe (**32**: C_s)	403.42	–191.62	211.80	196.12	C=C
PhOH (**33**: C_s)	379.94	–187.07	192.87	215.05	C_6H_5
H_2C=O (**34**: C_{2v})	404.32	–837.03	–432.71	840.64	C=O
HC(=O*)OH (**35**: C_s)	404.18	–508.34	–104.16	512.08	OC=O
HC(=O)O*H (**36**: C_s)	399.90	–301.91	97.99	309.94	OC=O

[a]Symmetry. [b]$-\Delta\sigma^{t}(O) = -[\sigma^{t}(O: S) - \sigma^{t}(O: O^{2-})]$.

Table S4. The σ^{d}(O), σ^{p}(O), σ^{t}(O) and $\Delta\sigma^{t}$(O) values for some oxygen species calculated with PBE0/BSS-A, together with the pre-α, α, β, γ and δ effects, corresponding to the $\Delta\sigma^{t}$(O) values.

Species (sym)[a]	σ^{d}(O)	σ^{p}(O)	σ^{t}(O)	$-\Delta\sigma^{t}$(O)[b]	effect
O^{2-} (**1**: O_h)	408.08	0.00	408.08	0.00	-
OH^- (**2**: $C_{\infty v}$)	396.19	–18.15	378.04	30.04	pre-α
MeO^- (**3**: C_{3v})	413.45	–113.93	299.52	108.56	α
EtO^- (**4**: C_s)	418.30	–257.84	160.46	247.62	β
i-PrO^- (**5**: C_s)	422.68	–271.53	151.15	256.93	β
t-BuO^- (**6**: C_s)	427.41	–214.47	212.94	195.14	β
H_2O (**7**: C_{2v})	392.53	–62.21	330.32	77.76	pre-α
MeOH (**8**: C_s)	394.94	–64.28	330.66	77.42	α
EtOH (**9**: C_s)	398.33	–99.45	298.88	109.19	β
i-PrOH (**10**: C_1)	403.69	–144.15	259.54	148.54	β
t-BuOH (**11**: C_s)	408.98	–173.05	235.93	172.15	β
n-PrOH (**12**: C_s)	402.23	–101.97	300.27	107.81	γ
n-BuOH (**13**: C_s)	405.74	–104.60	301.13	106.95	δ
Me_2O (**14**: C_{2v})	395.95	–62.20	333.75	74.33	α
EtOMe (**15**: C_s)	397.41	–93.69	303.72	104.36	β
i-PrOMe (**16**: C_1)	402.88	–117.04	285.84	122.24	β
t-BuOMe (**17**: C_s)	407.30	–130.64	276.67	131.41	β
n-PrOMe (**18**: C_s)	400.69	–94.63	306.06	102.02	γ
n-BuOMe (**19**: C_s)	405.00	–98.57	306.42	101.66	δ
Et_2O (**20**: C_{2v})	396.96	–123.92	273.04	135.04	β
i-Pr_2O (**21**: C_2)	406.04	–167.62	238.41	169.67	β
t-Bu_2O (**22**: C_2)	397.32	–184.59	212.73	195.35	β
n-Pr_2O (**23**: C_{2v})	396.84	–119.87	276.97	131.11	γ
n-Bu_2O (**24**: C_{2v})	406.09	–127.44	278.66	129.42	δ
H_3O^+ (**25**: C_{3v})	396.89	–88.78	308.11	99.97	pre-α
MeH_2O^+ (**26**: C_s)	400.29	–88.78	311.51	96.57	α
EtH_2O^+ (**27**: C_1)	408.30	–126.24	282.05	126.03	β
Me_3O^+ (**28**: C_{3v})	403.65	–95.20	308.45	99.63	α
Et_3O^+ (**29**: C_3)	398.56	–145.04	253.52	154.55	β
OH^+ (**30**: $C_{\infty v}$)	386.17	633.26	1019.42	–611.34	pre-α
H_2C=CHOH (**31**: C_s)	403.43	–187.68	215.75	192.33	C=C
H_2C=CHOMe (**32**: C_s)	402.83	–164.34	238.49	169.58	C=C
PhOH (**33**: C_s)	392.29	–178.60	213.69	194.39	C_6H_5
H_2C=O (**34**: C_{2v})	404.19	–826.92	–422.73	830.81	C=O
HC(=O*)OH (**35**: C_s)	404.40	–498.09	–93.69	501.77	OC=O
HC(=O)O*H (**36**: C_s)	399.88	–276.34	123.54	284.54	OC=O

[a]Symmetry. [b]$-\Delta\sigma^{t}(O) = -[\sigma^{t}(O: S) - \sigma^{t}(O: O^{2-})]$.

Table S5. The $\sigma^{d}(O)$, $\sigma^{p}(O)$, $\sigma^{t}(O)$ and $\Delta\sigma^{t}(O)$ values for some oxygen species calculated with LC-ωPBE/BSS-A, together with the pre-α, α, β, γ and δ effects, corresponding to the $\Delta\sigma^{t}(O)$ values.

Species (sym)[a]	$\sigma^{d}(O)$	$\sigma^{p}(O)$	$\sigma^{t}(O)$	$-\Delta\sigma^{t}(O)$[b]	effect
O^{2-} (**1**: O_h)	408.33	0.00	408.33	0.00	-
OH^- (**2**: $C_{\infty v}$)	395.94	–17.14	378.80	29.53	pre-α
MeO^- (**3**: C_{3v})	408.50	–75.88	332.62	75.71	α
EtO^- (**4**: C_s)	413.29	–164.30	248.99	159.34	β
i-PrO^- (**5**: C_s)	416.67	–193.72	222.95	185.38	β
t-BuO^- (**6**: C_s)	422.58	–188.98	233.60	174.73	β
H_2O (**7**: C_{2v})	392.54	–58.17	334.37	73.95	pre-α
MeOH (**8**: C_s)	393.98	–53.74	340.24	68.09	α
EtOH (**9**: C_s)	397.34	–86.90	310.43	97.89	β
i-PrOH (**10**: C_1)	403.14	–129.80	273.34	134.99	β
t-BuOH (**11**: C_s)	408.09	–159.48	248.61	159.72	β
n-PrOH (**12**: C_s)	400.74	–89.42	311.32	97.01	γ
n-BuOH (**13**: C_s)	404.41	–92.36	312.05	96.28	δ
Me_2O (**14**: C_{2v})	393.42	–46.13	347.28	61.04	α
EtOMe (**15**: C_s)	394.92	–75.29	319.62	88.70	β
i-PrOMe (**16**: C_1)	400.87	–98.54	302.33	106.00	β
t-BuOMe (**17**: C_s)	405.22	–113.20	292.02	116.31	β
n-PrOMe (**18**: C_s)	397.83	–76.86	320.97	87.36	γ
n-BuOMe (**19**: C_s)	401.99	–80.47	321.52	86.81	δ
Et_2O (**20**: C_{2v})	394.53	–103.69	290.84	117.49	β
i-Pr_2O (**21**: C_2)	404.45	–145.89	258.56	149.76	β
t-Bu_2O (**22**: C_2)	393.56	–161.77	231.79	176.54	β
n-Pr_2O (**23**: C_{2v})	394.14	–100.75	293.38	114.94	γ
n-Bu_2O (**24**: C_{2v})	402.03	–107.24	294.79	113.54	δ
H_3O^+ (**25**: C_{3v})	396.74	–85.72	311.02	97.30	pre-α
MeH_2O^+ (**26**: C_s)	399.72	–81.11	318.61	89.71	α
EtH_2O^+ (**27**: C_1)	407.12	–116.42	290.70	117.63	β
Me_3O^+ (**28**: C_{3v})	401.02	–75.76	325.26	83.06	α
Et_3O^+ (**29**: C_3)	398.89	–123.10	275.79	132.53	β
OH^+ (**30**: $C_{\infty v}$)	386.10	633.26	1019.36	–611.03	pre-α
H_2C=CHOH (**31**: C_s)	402.72	–170.64	232.08	176.25	C=C
H_2C=CHOMe (**32**: C_s)	400.96	–143.65	257.32	151.01	C=C
PhOH (**33**: C_s)	393.47	–165.13	228.35	179.98	C_6H_5
H_2C=O (**34**: C_{2v})	403.57	–824.81	–421.23	829.56	C=O
HC(=O*)OH (**35**: C_s)	404.25	–492.72	–88.47	496.80	OC=O
HC(=O)O*H (**36**: C_s)	399.49	–264.81	134.67	273.65	OC=O

[a]Symmetry. [b]$-\Delta\sigma^{t}(O) = -[\sigma^{t}(O: S) - \sigma^{t}(O: O^{2-})]$.

Table S6. The $\sigma^{d}(O)$, $\sigma^{p}(O)$, $\sigma^{t}(O)$ and $\Delta\sigma^{t}(O)$ values for some oxygen species calculated with ωB97X-D/BSS-A, together with the pre-α, α, β, γ and δ effects, corresponding to the $\Delta\sigma^{t}(O)$ values.

Species (sym)[a]	$\sigma^{d}(O)$	$\sigma^{p}(O)$	$\sigma^{t}(O)$	$-\Delta\sigma^{t}(O)$[b]	effect
O^{2-} (**1**: O_h)	408.28	0.00	408.28	0.00	-
OH^- (**2**: $C_{\infty v}$)	393.83	–16.13	377.70	30.58	pre-α
MeO^- (**3**: C_{3v})	408.87	–98.89	309.98	98.29	α
EtO^- (**4**: C_s)	412.97	–205.30	207.67	200.61	β
i-PrO^- (**5**: C_s)	415.56	–228.54	187.02	221.25	β
t-BuO^- (**6**: C_s)	420.29	–203.86	216.43	191.84	β
H_2O (**7**: C_{2v})	392.54	–61.18	331.37	76.91	pre-α
MeOH (**8**: C_s)	392.52	–59.57	332.95	75.32	α
EtOH (**9**: C_s)	395.10	–92.55	302.54	105.73	β
i-PrOH (**10**: C_1)	399.40	–135.01	264.39	143.88	β
t-BuOH (**11**: C_s)	402.04	–162.09	239.96	168.32	β
n-PrOH (**12**: C_s)	398.62	–94.97	303.65	104.62	γ
n-BuOH (**13**: C_s)	401.25	–96.89	304.37	103.91	δ
Me_2O (**14**: C_{2v})	390.93	–54.36	336.58	71.70	α
EtOMe (**15**: C_s)	391.86	–83.91	307.94	100.33	β
i-PrOMe (**16**: C_1)	396.00	–106.24	289.76	118.52	β
t-BuOMe (**17**: C_1)	399.03	–118.47	280.55	127.72	β
n-PrOMe (**18**: C_s)	394.94	–85.21	309.73	98.54	γ
n-BuOMe (**19**: C_s)	398.34	–88.04	310.31	97.97	δ
Et_2O (**20**: C_{2v})	391.27	–112.90	278.37	129.91	β
i-Pr_2O (**21**: C_2)	393.89	–149.80	244.10	164.18	β
t-Bu_2O (**22**: C_2)	381.15	–166.47	214.68	193.60	β
n-Pr_2O (**23**: C_2)	392.16	–110.33	281.83	126.45	γ
n-Bu_2O (**24**: C_2)	400.23	–116.90	283.33	124.95	δ
H_3O^+ (**25**: C_{3v})	404.04	–95.91	308.14	100.14	pre-α
MeH_2O^+ (**26**: C_s)	402.89	–89.40	313.50	94.78	α
EtH_2O^+ (**27**: C_1)	409.40	–124.15	285.26	123.02	β
Me_3O^+ (**28**: C_{3v})	396.57	–84.38	312.19	96.08	α
Et_3O^+ (**29**: C_3)	391.52	–130.29	261.23	147.05	β
OH^+ (**30**: $C_{\infty v}$)	388.03	1407.40	1795.43	–1387.15	pre-α
H_2C=CHOH (**31**: C_s)	401.63	–179.05	222.58	185.69	C=C
H_2C=CHOMe (**32**: C_s)	398.71	–135.81	262.90	145.38	C=C
PhOH (**33**: C_s)	393.62	–173.13	220.49	187.79	C_6H_5
H_2C=O (**34**: C_{2v})	404.53	–824.59	–420.07	828.34	C=O
HC(=O*)OH (**35**: C_s)	404.60	–497.59	–92.99	501.26	OC=O
HC(=O)O*H (**36**: C_s)	399.22	–271.31	127.91	280.37	OC=O

[a]Symmetry. [b]$-\Delta\sigma^{t}(O) = -[\sigma^{t}(O: S) - \sigma^{t}(O: O^{2-})]$.

Table S7. The σ^t(O) and $-\Delta\sigma^t_{Me_2O}$(O) values for some ether species calculated with MP2/BSS-A, together with observed values.[a]

Species (sym[b])	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
I (monomeric ethers)			
Me_2O (C_{2v})	354.80	–52.5	–52.5
EtOMe (C_s)	324.65	–22.4	–22.5
n-PrOMe (C_s)	329.27	–27.0	–28.5
i-PrOMe (C_1)	313.05	–10.8	–2.0
n-BuOMe (C_s)	327.70	–25.4	–28.5
i-BuOMe (C_1)	326.68	–24.4	–30.0
s-BuOMe (C_1)	328.73	–26.4	–8.5
t-BuOMe (C_s)	293.48	8.8	8.5
n-PeOMe (C_s)	327.65	–25.4	–27.5
neo-PeOMe (C_s)	330.24	–27.9	–32.5
s-PeOMe (C_1)	303.23	-0.9	–16.5
i-PeOMe (C_1)	332.79	–30.5	–29.5
neo-HexOMe (C_s)	328.54	–26.2	–29.5
Et_2O (C_{2v})	291.82	10.5	6.5
n-PrOEt (C_s)	297.26	5.0	1.7
i-PrOEt (C_1)	279.19	23.1	28.0
n-BuOEt (C_s)	295.60	6.7	–1.5
i-BuOEt (C_1)	294.59	7.7	–1.0
s-BuOEt (C_1)	295.47	6.8	24.5
t-BuOEt (C_1)	258.76	43.5	40.5
n-PeOEt (C_s)	295.54	6.8	1.5
neo-PeOEt (C_s)	298.38	3.9	–3.5
s-PeOEt (C_1)	269.79	32.5	15.0
n-Pr_2O (C_{2v})	302.79	–0.5	–3.5
n-PrO*i*-Pr (C_1)	281.10	21.2	24.0
i-Pr_2O (C_2)	258.88	43.4	52.5
i-PrO*t*-Bu (C_1)	242.24	60.1	62.5
n-Bu_2O (C_{2v})	299.45	2.8	–7.0[e]
s-Bu_2O (C_2)	268.23	34.1	41.5
t-Bu_2O (C_2)	224.81	77.5	76.0
i-Pe_2O (C_2)	310.44	–8.1	–7.0[e]

[a]Calculated with the GIAO (MP2) method under MP2/6-311++G(3df,3pd) (MP2/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C.

Table S8. The σ^t(O) and $-\Delta\sigma^t_{Me_2O}$ (O) values for some ether species calculated with B3LPY/def2TZVP, together with observed values.[a]

Species (sym[b])	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
I (monomeric ethers)			
Me_2O (C_{2v})	322.43	–52.5	–52.5
EtOMe (C_s)	292.19	–22.3	–22.5
n-PrOMe (C_s)	294.82	–24.9	–28.5
i-PrOMe (C_1)	281.97	–12.0	–2.0
n-BuOMe (C_s)	295.58	–25.7	–28.5
i-BuOMe (C_1)	295.32	–25.4	–30.0
s-BuOMe (C_1)	297.88	–27.9	–8.5
t-BuOMe (C_s)	263.62	6.3	8.5
n-PeOMe (C_s)	295.31	–25.4	–27.5
neo-PeOMe (C_s)	297.75	–27.8	–32.5
s-PeOMe (C_1)	272.31	–2.4	–16.5
i-PeOMe (C_1)	298.86	–28.9	–29.5
neo-HexOMe (C_s)	299.37	–29.4	–29.5
Et_2O (C_{2v})	260.28	9.7	6.5
n-PrOEt (C_s)	262.95	7.0	1.7
i-PrOEt (C_1)	249.16	20.8	28.0
n-BuOEt (C_s)	263.81	6.1	–1.5
i-BuOEt (C_1)	263.50	6.4	–1.0
s-BuOEt (C_1)	264.84	5.1	24.5
t-BuOEt (C_1)	229.69	40.2	40.5
n-PeOEt (C_s)	263.69	6.2	1.5
neo-PeOEt (C_s)	266.14	3.8	–3.5
s-PeOEt (C_1)	239.32	30.6	15.0
n-Pr_2O (C_{2v})	265.19	4.7	–3.5
n-PrO*i*-Pr (C_1)	251.87	18.1	24.0
i-Pr_2O (C_2)	227.13	42.8	52.5
i-PrO*t*-Bu (C_1)	212.37	57.6	62.5
n-Bu_2O (C_{2v})	266.99	2.9	–7.0[e]
s-Bu_2O (C_2)	218.08	51.8	41.5
t-Bu_2O (C_2)	196.23	73.7	76.0
i-Pe_2O (C_2)	273.75	–3.8	–7.0[e]

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/def2TZVP. [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C.

Table S9. σ^{d}(O), σ^{p}(O), σ^{t}(O) and $-\Delta\sigma^{t}_{Me_2O}$(O) values of various isomer species with its energies calculated by using B3LYP/BSS-A.

Species (sym)[a]		*Energy*/au	σ^{d}(O)	σ^{p}(O)	σ^{t}(O)	$-\Delta\sigma^{t}$(O)[b]
n-PrOMe (**18**)						
18$_{anti}$	(C_s)	–233.749331	400.83	–105.99	294.84	113.48
18$_{gauche}$	(C_1)	–233.749329	397.22	–100.14	297.08	113.24
n-BuOMe (**19**)						
19$_{anti}$	(C_s)	–273.076373	405.13	–110.00	295.13	113.19
19$_{gauche}$	(C_1)	–273.076479	397.94	–102.51	295.43	112.90
n-Pr_2O (**23**)						
23$_{anti}$	(C_{2v})	–312.408573	397.47	–132.00	265.47	142.86
23$_{gauche}$	(C_2)	–312.408461	391.57	–120.22	271.35	136.98
n-Bu_2O (**24**)						
24$_{anti}$	(C_{2v})	–391.062646	407.04	–140.02	267.02	141.31
24$_{gauche}$	(C_2)	–391.062769	393.26	–124.74	268.52	139.81

[a]Symmetry. [b]$-\Delta\sigma^{t}(O) = -[\sigma^{t}(O{:}\ S) - \sigma^{t}(O{:}\ O^{2-})]$.

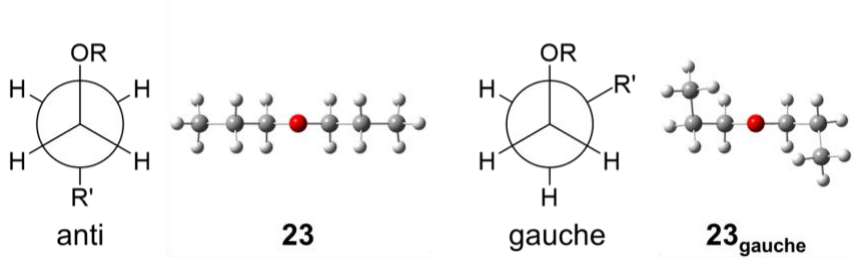

Table S10. The σ^t(O) and $-\Delta\sigma^t_{Me_2O}$(O) values (ppm) for some oxygen monomeric and dimeric species, together with observed values with the solvent effect of $CHCl_3$.[a]

Species (sym[b])	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
I (monomeric ethers)			
Me_2O (C_{2v})	325.20	–52.5	–52.5
EtOMe (C_s)	294.08	–21.4	–22.5
n-PrOMe (C_s)	296.93	–24.2	–28.5
i-PrOMe (C_1)	275.47	–2.8	–2.0
n-BuOMe (C_s)	297.51	–24.8	–28.5
i-BuOMe (C_1)	297.50	–24.8	–30.0
s-BuOMe (C_1)	281.45	–8.7	–8.5
t-BuOMe (C_s)	264.57	8.1	8.5
n-PeOMe (C_s)	298.21	–25.5	–27.5
neo-PeOMe (C_s)	300.96	–28.3	–32.5
s-PeOMe (C_1)	280.01	–7.3	–16.5
i-PeOMe (C_1)	301.36	–28.7	–29.5
neo-HexOMe (C_s)	300.81	–28.1	–29.5
Et_2O (C_{2v})	262.31	10.4	6.5
n-PrOEt (C_s)	264.19	8.5	1.7
i-PrOEt (C_1)	242.35	30.4	28.0
n-BuOEt (C_s)	266.15	6.6	–1.5
i-BuOEt (C_1)	265.56	7.1	–1.0
s-BuOEt (C_1)	248.33	24.4	24.5
t-BuOEt (C_1)	230.26	42.4	40.5
n-PeOEt (C_s)	265.69	7.0	1.5
neo-PeOEt (C_s)	269.58	3.1	–3.5
s-PeOEt (C_1)	247.20	25.5	15.0
n-Pr_2O (C_{2v})	267.13	5.6	–3.5
n-PrO*i*-Pr (C_1)	244.72	28.0	24.0
i-Pr_2O (C_2)	224.72	48.0	52.5
i-PrO*t*-Bu (C_1)	209.62	63.1	62.5
n-Bu_2O (C_{2v})	270.21	2.5	–7.0[e]
s-Bu_2O (C_2)	235.98	36.7	41.5
t-Bu_2O (C_2)	196.82	75.9	76.0
i-Pe_2O (C_2)	275.48	–2.8	–7.0[e]

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C.

(**Table S10** continued)

Species (sym[b])	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
(Me_2O (C_{2v})	325.20	–52.5	–52.5)
II (monomeric alcohols)			
MeOH (C_s)	327.13	–54.4	–37
EtOH (C_s)	294.41	–21.7	6
n-PrOH (C_s)	296.20	–23.5	0
i-PrOH (C_1)	255.91	16.8	38
n-BuOH (C_s)	296.98	–24.3	–4
i-BuOH (C_1)	297.22	–24.5	**–2**
s-BuOH (C_1)	261.70	11.0	**34**
t-BuOH (C_s)	231.46	41.2	70
n-PeOH (C_s)	296.73	–24.0	–7
III (monomeric carboxylic acids)			
HC(=O)OH (C_s)	15.45[f]	257.3	253[g]
=O	-82.86		
–OH	113.76		
MeC(=O)OH (C_s)	15.36[f]	257.3	251[g]
=O	-85.09		
–OH	115.81		
EtC(=O)OH (C_s)	22.39[f]	250.3	244[g]
=O	-74.74		
–OH	119.52		
i-PrC(=O)OH (C_1)	25.72[f]	247.0	242[g]
=O	-66.23		
–OH	117.67		
t-BuC(=O)OH (C_s)	24.16[f]	248.5	240[g,h]
=O	-73.37		
–OH	121.70		

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 ℃, pure liquids. [e]Measured at 100 ℃. [f]σ^t(O) was given as the average value of the oxygen at the carbonyl and hydroxy groups. [g]Due to rapid proton exchange, only one peak appeared. [h]Measured at 40 ℃.

(**Table S10** continued)

Species (sym[b])		σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
cf:				
Me_2O (C_1)		561.36	–51.1	–52.5
	Unit 1	322.57		
	Unit 2	320.04		
IV (dimeric alcohols)				
MeOH (C_1)		325.08	–52.4	–37
	Acceptor	319.79		
	Donor	330.36		
EtOH (C_1)		288.60	–15.9	6
	Acceptor	287.91		
	Donor	289.29		
n-PrOH (C_1)		290.61	–17.9	0
	Acceptor	289.53		
	Donor	291.70		
i-PrOH (C_1)		251.49	21.2	38
	Acceptor	248.39		
	Donor	254.59		
n-BuOH (C_1)		291.42	–18.7	–4
	Acceptor	290.06		
	Donor	292.78		
i-BuOH (C_1)		292.42	–19.7	–2
	Acceptor	290.55		
	Donor	294.29		
s-BuOH (C_1)		259.27	13.4	34
	Acceptor	256.10		
	Donor	262.43		
t-BuOH (C_1)		226.22	46.5	70
	Acceptor	222.05		
	Donor	230.39		
n-PeOH (C_1)		291.27	–18.6	–7
	Acceptor	290.17		
	Donor	292.38		

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids.

(**Table S10** continued)

Species (sym[b])	σ^t(O)	$-\Delta\sigma^t_{Me_2O}$(O)[c]	δ(O)[d]
V (dimeric carboxylic acids)			
HC(=O)OH (C_s)	23.96[f]	248.7	253[g]
Acceptor	–47.52		
Donor	95.44		
MeC(=O)OH (C_{2h})	26.30[f]	246.4	251[g]
Acceptor	–48.42		
Donor	101.03		
EtC(=O)OH (C_{2h})	32.67[f]	240.0	244[g]
Acceptor	–39.75		
Donor	105.09		
i-PrC(=O)OH (C_i)[i]	36.65[f]	236.1	242[g]
Acceptor	–28.81		
Donor	102.11		
t-BuC(=O)OH (C_{2h})[i]	35.48[f]	237.2	240[g,h]
Acceptor	–37.57		
Donor	108.53		

[a]Calculated with the GIAO-DFT (B3LYP) method under B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-A). [b]Symmetry. [c]$-\Delta\sigma^t_{Me_2O}(O) = -[\sigma^t(O{:}\ S) - \sigma^t(O{:}\ Me_2O)] - 52.5$. [d]Observed values taken from Refs. S1–S5, unless otherwise noted. Measured at 25 °C, pure liquids. [e]Measured at 100 °C. [f]σ^t(O) was given as the average value of the oxygen at the carbonyl and hydroxy groups. [g]Due to rapid proton exchange, only one peak appeared. [h]Measured at 40 °C. [i]The optimization was conducted with tight convergence criteria and an ultrafine grid.

Table S11. Parameters for **1**–**36** of regression lines ($\sigma^{t}_{functional} = a \bullet \sigma^{t}_{B3LYP} + b$), except OH^{+} (**30**) and values of R^2 for each functional over the basis set as BSS-A.

Functional	*a*	*b*	R_c^2	MAE	max. AE
CAM-B3LYP	0.9979	13.73	0.9930	13.47	63.17 (EtO^{-})
PBE	1.0145	–17.37	0.9889	14.33	84.09 (EtO^{-})
PBE0	0.9935	12.11	0.9983	10.61	31.54 (EtO^{-})
LC-*ω*PBE	0.9812	31.96	0.9750	27.59	120.08 (EtO^{-})
*ω*B97X-D	0.9822	21.21	0.9894	17.07	78.75 (EtO^{-})

Table S12. Parameters for various oxygen species of regression lines ($\delta = a \bullet \sigma^{t}_{functional} + b$) and values of R_c^2 for correlations of δ(O: S) versus $-\Delta\sigma^{t}_{Me2O}$(O: S) for each functional over the basis set as BSS-A[a,b].

Functional	*a*	*b*	R_c^2	MAE	max. AE
B3LYP	1.030	6.895	0.900	46.40	66.1 (*n*-Bu_2O)
CAM-B3LYP	1.078	6.037	0.926	39.26	58.1 (*n*-Bu_2O)
PBE	0.916	–5.077	0.877	55.16	76.0 (*n*-Bu_2O)
PBE0	1.077	6.958	0.924	39.87	58.7 (*n*-Bu_2O)
LC-*ω*PBE	1.156	8.581	0.950	29.54	46.6 (*n*-Bu_2O)
*ω*B97X-D	1.110	9.409	0.898	36.09	55.0 (*n*-Bu_2O)

[a]Species selected some alcohols and ethers which measured values exist, MeOH (**8**), EtOH (**9**), *i*-PrOH (**10**), *t*-BuOH (**11**), *n*-PrOH (**12**), *n*-BuOH (**13**), Me_2O (**14**), EtOMe (**15**), *i*-PrOMe (**16**), *t*-BuOMe (**17**), *n*-PrOMe (**18**), *n*-BuOMe (**19**), Et_2O (**20**), *i*-Pr_2O (**21**), *t*-Bu_2O (**22**), *n*-Pr_2O (**23**), *n*-Bu_2O (**24**) and CH_2=CHOMe (**32**). [b]Observed values taken from Refs. 1, 2 and 9 unless otherwise noted. Measured at 25 °C, pure liquids.

Table S13. The $\sigma^d(O)$, $\sigma^p(O)$, $\sigma^t(O)$ and $\Delta\sigma^t(O)$ values for some oxygen species calculated with B3LYP/6-311+G(3d,3p)//B3LYP/6-311++G(3df,3pd) (B3LYP/BSS-B//B3LYP/BSS-A), together with the pre-α, α, β, γ and δ effects, corresponding to the $-\Delta\sigma^t(O)$ values.

Species (sym)[a]	$\sigma^d(O)$	$\sigma^p(O)$	$\sigma^t(O)$	$-\Delta\sigma^t(O)$[b]	effect
O^{2-} (O_h)	408.29	0.00	408.29	0.00	---
OH^- ($C_{\infty v}$)	392.62	–30.73	361.89	46.40	pre-α
MeO^- (C_{3v})	400.59	–104.61	295.99	112.30	α
EtO^- (C_s)	410.89	–249.76	161.13	247.16	β
i-PrO^- (C_s)	423.45	–278.77	144.67	263.62	β
t-BuO^- (C_s)	437.53	–236.60	200.93	207.36	β
H_2O (C_{2v})	387.38	–61.88	325.50	82.79	pre-α
MeOH (C_s)	391.84	–71.40	320.44	87.85	α
EtOH (C_s)	399.61	–107.28	292.33	115.96	β
i-PrOH (C_1)	403.12	–153.69	249.42	158.87	β
t-BuOH (C_s)	415.38	–189.87	225.51	182.78	β
n-PrOH (C_s)	399.71	–109.58	290.13	118.16	γ
n-BuOH (C_s)	405.44	–114.48	290.95	117.34	δ
Me_2O (C_{2v})	398.00	–77.31	320.69	87.60	α
EtOMe (C_s)	401.99	–111.82	290.17	118.12	β
i-PrOMe (C_1)	407.03	–135.15	271.88	136.41	β
t-BuOMe (C_s)	413.86	–151.36	262.50	145.79	β
n-PrOMe (C_s)	407.69	–114.21	293.48	114.81	γ
n-BuOMe (C_s)	413.98	–120.71	293.27	115.02	δ
Et_2O (C_{2v})	405.93	–145.88	260.06	148.23	β
i-Pr_2O (C_2)	408.05	–185.47	222.58	185.71	β
t-Bu_2O (C_2)	403.82	–208.74	195.08	213.21	β
n-Pr_2O (C_{2v})	411.26	–146.93	264.33	143.96	γ
n-Bu_2O (C_{2v})	420.03	–153.88	266.15	142.14	δ
H_3O^+ (C_{3v})	391.75	–88.37	303.38	104.91	pre-α
MeH_2O^+ (C_s)	399.18	–95.08	304.10	104.19	α
EtH_2O^+ (C_1)	407.96	–133.32	274.64	133.65	β
Me_3O^+ (C_{3v})	428.83	–133.83	295.01	113.28	α
Et_3O^+ (C_3)	440.97	–203.75	237.22	171.07	β
OH^+ ($C_{\infty v}$)	384.99	1021.20	1406.19	–997.90	pre-α
H_2C=CHOH (C_s)	402.08	–194.59	207.50	200.79	C=C
H_2C=CHOMe (C_s)	402.95	–176.48	226.46	181.83	C=C
PhOH (C_s)	386.96	–180.13	206.83	201.46	C_6H_5
H_2C=O (C_{2v})	396.79	–824.78	–427.99	836.28	C=O
HC(=O*)OH (C_s)	396.45	–497.88	–101.43	509.72	OC=O
HC(=O)O*H (C_s)	397.93	–284.07	113.86	294.43	OC=O

[a]Symmetry. [b]$-\Delta\sigma^t(O) = -[\sigma^t(O: S) - \sigma^t(O: O^{2-})]$.

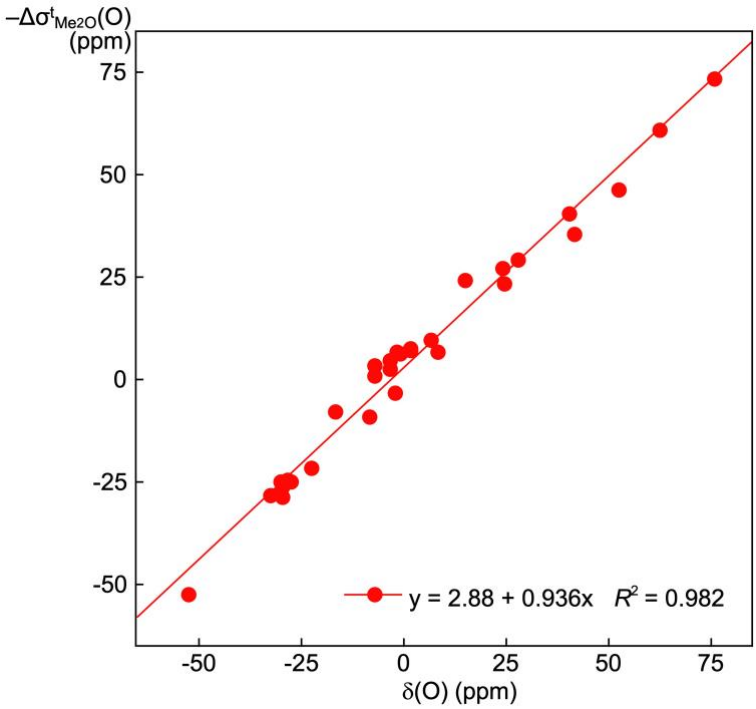

Fig. S1 Plot of observed values (δ) versus calculated chemical shift values [–Δσ^t(O)] under B3LYP/BSS-A.

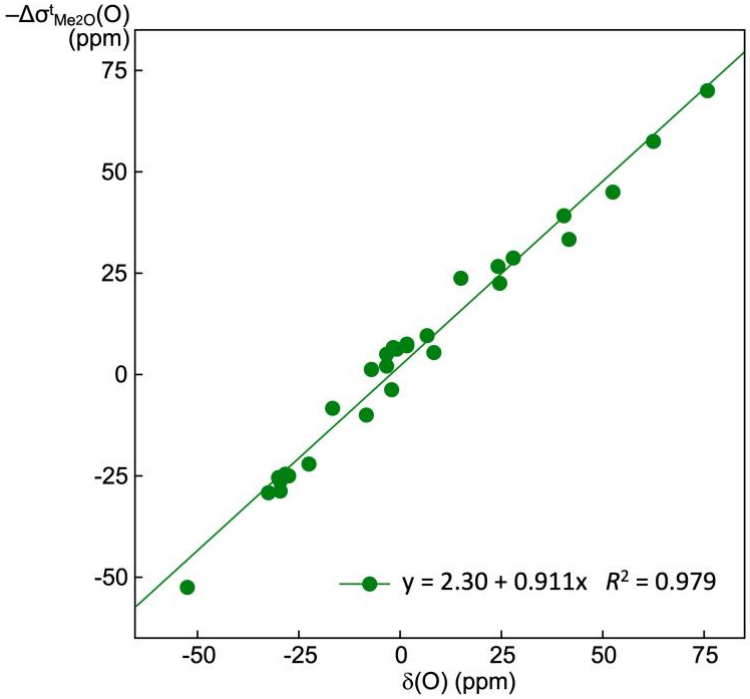

Fig. S2 Plot of observed values (δ) versus calculated chemical shift values [–Δσ^t(O)] under CAM-B3LYP/BSS-A.

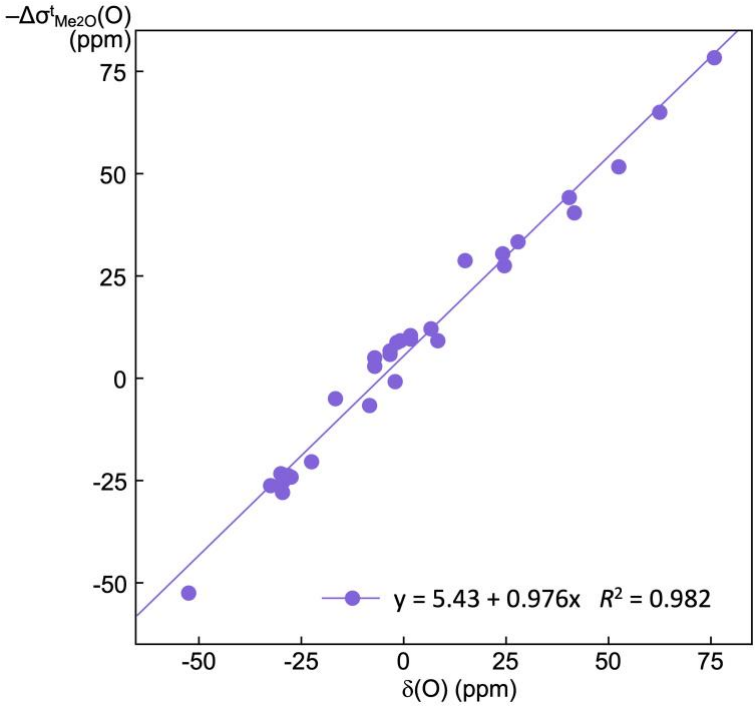

Fig. S3 Plot of observed values (δ) versus calculated chemical shift values [$-\Delta\sigma^{t}$(O)] under PBE/BSS-A.

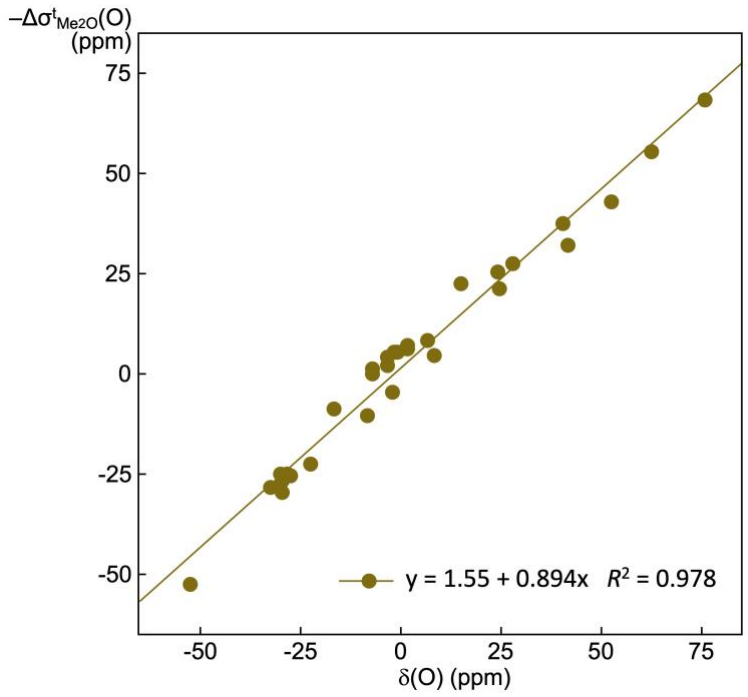

Fig. S4 Plot of observed values (δ) versus calculated chemical shift values [$-\Delta\sigma^{t}$(O)] under PBE0/BSS-A.

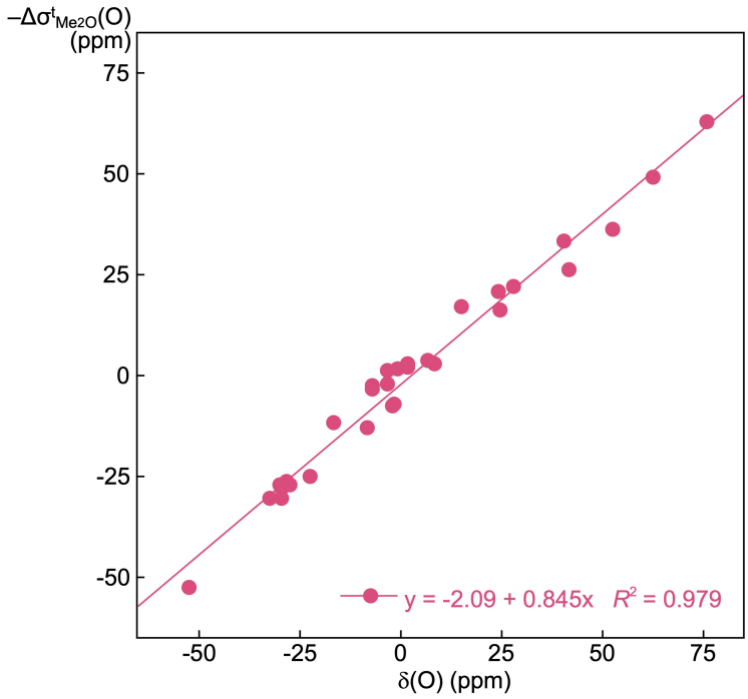

Fig. S5 Plot of observed values (δ) versus calculated chemical shift values [–Δσ^t(O)] under LC-*ω*PBE/BSS-A.

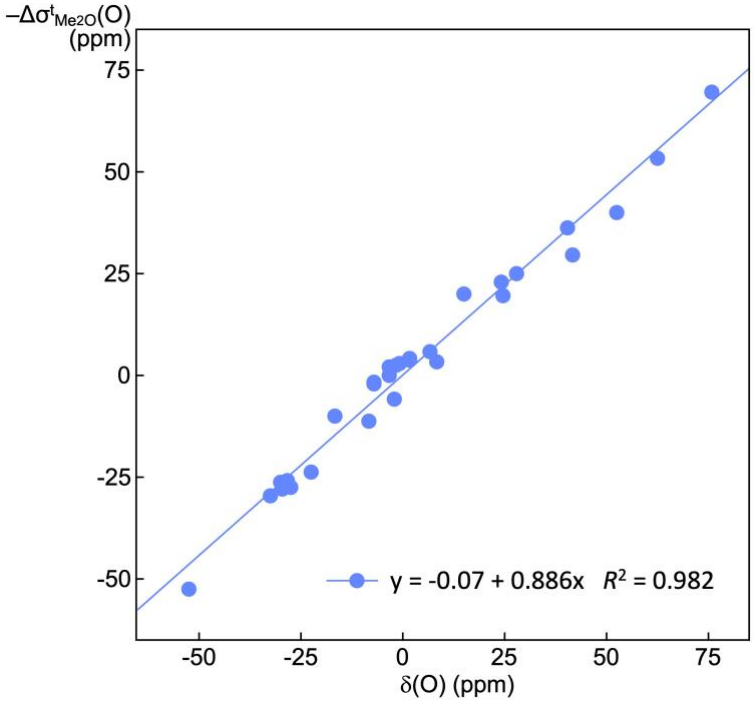

Fig. S6 Plot of observed values (δ) versus calculated chemical shift values [–Δσ^t(O)] under *ω*B97X-D/BSS-A.

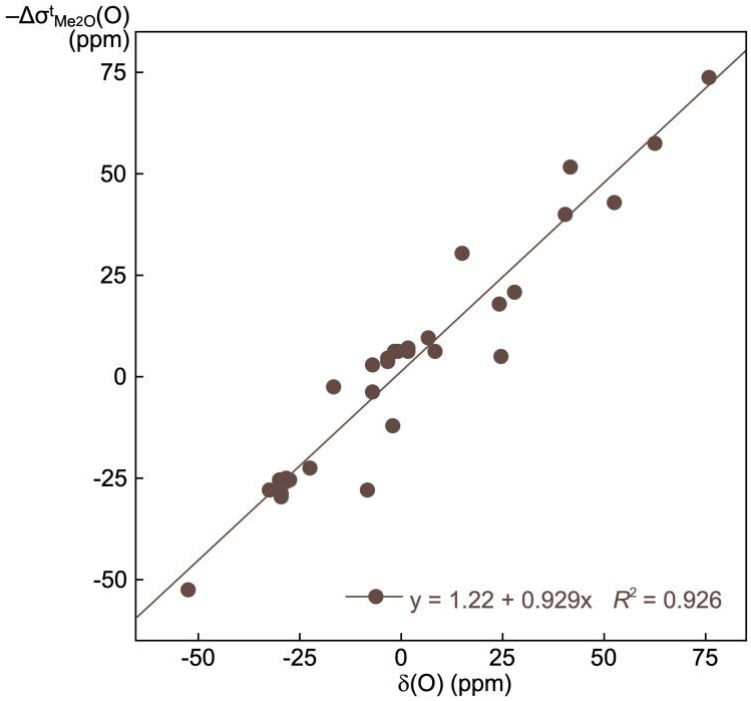

Fig. S7 Plot of observed values (δ) versus calculated chemical shift values [–Δσ^t(O)] under B3LYP/def2TZVP.

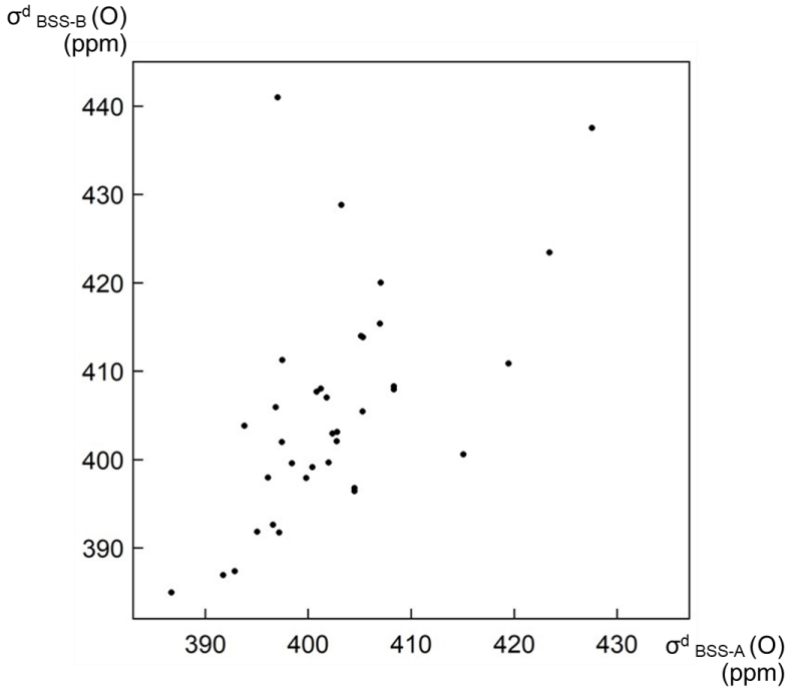

Fig. S8 Plot of σ^d(O) calculated under B3LYP/BSS-B//B3LYP/BSS-A versus those under B3LYP/BSS-A.

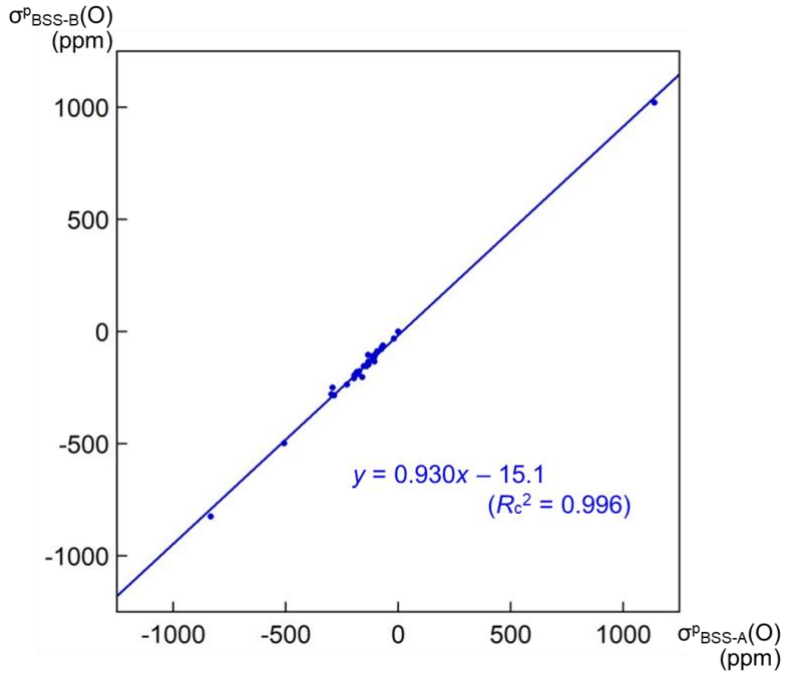

Fig. S9 Plot of σ^{p}(O) calculated under B3LYP/BSS-B//B3LYP/BSS-A versus those under B3LYP/BSS-A.

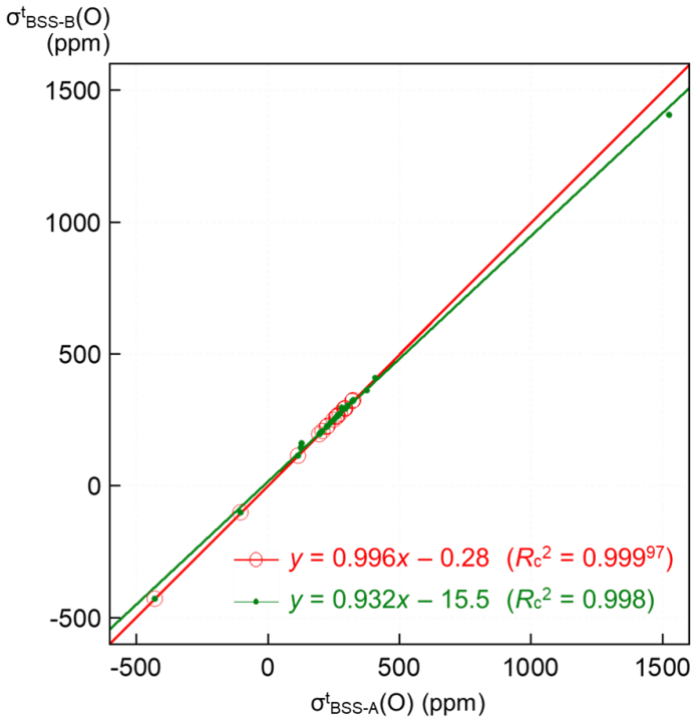

Fig. S10 Plot of σ^{t}(O) calculated under B3LYP/BSS-B//B3LYP/BSS-A versus those under B3LYP/BSS-A. All data are shown by green dots and those in neutral species by red circles.

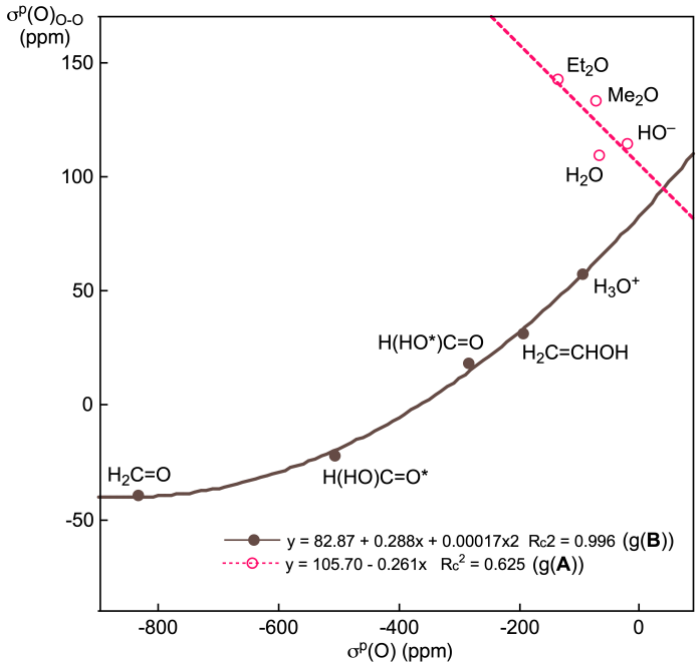

Fig. S11 Plots of $\sigma^{p}(O)_{o\text{-}o}$ versus $\sigma^{p}(O)$ under B3LYP/BSS-A. The correlations were poor for g(**A**) ($y = 105.70 - 0.261x$: $R_c^2 = 0.625$) and very good for g(**B**) ($y = 82.87 + 0.288x + 0.00017x^2$: $R_c^2 = 0.996$).

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S5. G. A. Kalabin, D. F. Kushnarev, R. B. Valeyev, B. A. Trofimov, and M. A. Fedotov, *Org. Magn. Reson.* **1982**, *18*, 1–9. (Chemical shifts of methyl vinyl ether. CCl_4 was used as a solvent.)

Optimized structures given by Cartesian coordinates

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies with the B3LYP/BSS-A method of the Gaussian 09 program.

Compound **1**: O^{2-}
Symmetry O_h
energy E_h = –74.8820358 au
Standard orientation

8	0	0.000000	0.000000	0.000000

Compound **2**: OH^-
Symmetry $C_{\infty v}$
energy E_h = –75.8309271 au
Standard orientation

8	0	0.000000	0.000000	0.107170
1	0	0.000000	0.000000	–0.857363

Compound **3**: MeO^-
Symmetry C_{3v}
energy E_h = –115.1550451 au
Standard orientation

8	0	0.000000	0.000000	0.791502
6	0	0.000000	0.000000	–0.538646
1	0	0.000000	1.024442	–1.033380
1	0	0.887193	–0.512221	–1.033380
1	0	–0.887193	–0.512221	–1.033380

Compound **4**: EtO^-
Symmetry C_s
energy E_h = –154.4932382 au
Standard orientation

8	0	1.283141	0.182701	0.000000
6	0	0.000000	0.529780	0.000000
1	0	–0.319422	1.162009	0.887805
1	0	–0.319422	1.162009	–0.887805
6	0	–0.992125	–0.673051	0.000000
1	0	–2.041667	–0.338697	0.000000
1	0	–0.815935	–1.293652	–0.884326
1	0	–0.815935	–1.293652	0.884326

Compound **5**: *i*-PrO^-
Symmetry C_s
energy E_h = –193.8283326 au
Standard orientation

8	0	–0.779002	1.197836	0.000000
6	0	0.211763	0.309037	0.000000

1	0	1.247678	0.777870	0.000000
6	0	0.211763	–0.607462	1.264972
1	0	1.056888	–1.310878	1.286931
1	0	0.254724	0.022394	2.156380
1	0	–0.725311	–1.174133	1.299150
6	0	0.211763	–0.607462	–1.264972
1	0	0.254724	0.022394	–2.156380
1	0	1.056888	–1.310878	–1.286931
1	0	–0.725311	–1.174133	–1.299150

Compound **6**: *t*-BuO$^-$
Symmetry C_s
energy E_h = –233.1599602 au
Standard orientation

8	0	–0.526876	1.388220	0.000000
6	0	–0.052669	0.138394	0.000000
6	0	1.515499	0.111495	0.000000
1	0	1.945881	–0.899894	0.000000
1	0	1.873384	0.646704	0.882969
1	0	1.873384	0.646704	–0.882969
6	0	–0.526876	–0.664000	–1.261469
1	0	–1.619446	–0.680132	–1.274613
1	0	–0.156890	–1.698389	–1.299135
1	0	–0.189720	–0.136782	–2.157332
6	0	–0.526876	–0.664000	1.261469
1	0	–0.156890	–1.698389	1.299135
1	0	–1.619446	–0.680132	1.274613
1	0	–0.189720	–0.136782	2.157332

Compound **7**: H_2O
Symmetry C_{2v}
energy E_h = – 76.4645116 au
Standard orientation

8	0	0.000000	0.000000	0.116966
1	0	0.000000	0.762733	–0.467862
1	0	0.000000	–0.762733	–0.467862

Compound **8**: MeOH
Symmetry C_s
energy E_h = –115.7743176 au
Standard orientation

8	0	–0.046432	–0.756172	0.000000
1	0	0.860988	–1.069539	0.000000
6	0	–0.046432	0.664807	0.000000
1	0	–1.087885	0.979086	0.000000
1	0	0.438471	1.075495	0.890506
1	0	0.438471	1.075495	–0.890506

Compound **9**: EtOH
Symmetry C_s
energy E_h = –155.1069850 au
Standard orientation

8	0	1.199571	–0.220624	0.000000
1	0	1.956528	0.370387	0.000000
6	0	0.000000	0.553198	0.000000
1	0	–0.036611	1.198023	0.885108
1	0	–0.036611	1.198023	–0.885108
6	0	–1.176707	–0.400020	0.000000
1	0	–2.115206	0.155466	0.000000
1	0	–1.152212	–1.037988	–0.883334
1	0	–1.152212	–1.037988	0.883334

Compound **10**: *i*-PrOH
Symmetry C_1
energy E_h = –194.4391735 au
Standard orientation

8	0	0.052530	1.370704	–0.162761
1	0	0.886106	1.774640	0.093759
6	0	–0.001740	0.038904	0.361903
1	0	0.006374	0.088076	1.458292
6	0	–1.328476	–0.547372	–0.089136
1	0	–1.366229	–0.603917	–1.177868
1	0	–1.462727	–1.550533	0.316038
1	0	–2.154529	0.076636	0.249535
6	0	1.193395	–0.785970	–0.102691
1	0	2.132425	–0.333451	0.223289
1	0	1.152235	–1.795299	0.309800
1	0	1.207026	–0.855157	–1.191208

Compound **11**: *t*-BuOH
Symmetry C_s
energy E_h = –233.7696130 au
Standard orientation

8	0	0.486018	1.368146	0.000000
1	0	1.447835	1.351257	0.000000
6	0	–0.001335	0.013541	0.000000
6	0	0.486018	–0.705446	1.261292
1	0	0.098006	–1.723809	1.310195
1	0	1.576739	–0.764086	1.276189
1	0	0.161121	–0.167461	2.151414
6	0	0.486018	–0.705446	–1.261292
1	0	0.098006	–1.723809	–1.310195
1	0	0.161121	–0.167461	–2.151414
1	0	1.576739	–0.764086	–1.276189

6	0	–1.521713	0.143320	0.000000
1	0	–1.993801	–0.839102	0.000000
1	0	–1.853912	0.688784	0.882843
1	0	–1.853912	0.688784	–0.882843

Compound **12**: *n*-PrOH
Symmetry C_s
energy E_h = –194.4339571 au
Standard orientation

8	0	–1.472735	–1.140396	0.000000
1	0	–1.544507	–2.097938	0.000000
6	0	–0.094374	–0.773020	0.000000
1	0	0.410194	–1.177714	0.885536
1	0	0.410194	–1.177714	–0.885536
6	0	0.000000	0.741864	0.000000
1	0	–0.529661	1.122253	–0.875906
1	0	–0.529661	1.122253	0.875906
6	0	1.445483	1.236592	0.000000
1	0	1.485476	2.325672	0.000000
1	0	1.986596	0.886870	0.881330
1	0	1.986596	0.886870	–0.881330

Compound **13**: *n*-BuOH
Symmetry C_s
energy E_h = –233.7610000 au
Standard orientation

8	0	–2.369922	0.650027	0.000000
1	0	–3.230208	0.223416	0.000000
6	0	–1.351247	–0.349361	0.000000
1	0	–1.444029	–0.989255	0.885519
1	0	–1.444029	–0.989255	–0.885519
6	0	0.000000	0.341935	0.000000
1	0	0.058038	0.992537	–0.876439
1	0	0.058038	0.992537	0.876439
6	0	1.171611	–0.640385	0.000000
1	0	1.099355	–1.293560	0.874612
1	0	1.099355	–1.293560	–0.874612
6	0	2.532109	0.055462	0.000000
1	0	3.348251	–0.667889	0.000000
1	0	2.649882	0.689457	–0.880648
1	0	2.649882	0.689457	0.880648

Compound **14**: Me_2O
Symmetry C_{2v}
energy E_h = –155.0899217 au
Standard orientation

8	0	0.000000	0.000000	0.584953

6	0	0.000000	1.174583	–0.194140
1	0	0.000000	2.019927	0.490609
1	0	0.890029	1.232286	–0.832789
1	0	–0.890029	1.232286	–0.832789
6	0	0.000000	–1.174583	–0.194140
1	0	0.890029	–1.232286	–0.832789
1	0	0.000000	–2.019927	0.490609
1	0	–0.890029	–1.232286	–0.832789

Compound **15**: EtOMe
Symmetry C_s
energy E_h = –194.4224628 au
Standard orientation

8	0	–0.013326	–0.709585	0.000000
6	0	–1.313401	–1.252848	0.000000
1	0	–1.214437	–2.336309	0.000000
1	0	–1.877323	–0.946764	0.889759
1	0	–1.877323	–0.946764	–0.889759
6	0	0.000000	0.706265	0.000000
1	0	–0.532428	1.082090	0.884561
1	0	–0.532428	1.082090	–0.884561
6	0	1.437271	1.184095	0.000000
1	0	1.962293	0.821609	–0.883391
1	0	1.472742	2.274051	0.000000
1	0	1.962293	0.821609	0.883391

Compound **16**: *i*-PrOMe
Symmetry C_1
energy E_h = –233.7520523 au
Standard orientation

8	0	–0.707122	–0.561873	–0.363852
6	0	–1.962524	–0.108641	0.090631
1	0	–2.129166	0.951887	–0.124108
1	0	–2.719754	–0.689471	–0.432343
1	0	–2.077739	–0.268106	1.169808
6	0	0.420758	–0.006993	0.311746
1	0	0.225312	–0.042576	1.393043
6	0	1.603336	–0.907555	–0.007811
1	0	1.796083	–0.909186	–1.081421
1	0	2.501033	–0.558912	0.503274
1	0	1.399709	–1.930920	0.304330
6	0	0.675531	1.442528	–0.097666
1	0	0.866601	1.502214	–1.170040
1	0	–0.171978	2.086062	0.136558
1	0	1.544270	1.837964	0.430319

Compound **17**: *t*-BuOMe

Symmetry C_s
energy E_h = –273.0790274 au
Standard orientation

8	0	0.441581	–1.033499	0.000000
6	0	–0.633856	–1.946981	0.000000
1	0	–0.189822	–2.940725	0.000000
1	0	–1.264786	–1.853294	0.889245
1	0	–1.264786	–1.853294	–0.889245
6	0	0.141161	0.376056	0.000000
6	0	–0.633856	0.771595	–1.262442
1	0	–1.636154	0.343805	–1.277241
1	0	–0.741048	1.855383	–1.313001
1	0	–0.101787	0.437928	–2.153499
6	0	–0.633856	0.771595	1.262442
1	0	–0.101787	0.437928	2.153499
1	0	–0.741048	1.855383	1.313001
1	0	–1.636154	0.343805	1.277241
6	0	1.519225	1.036303	0.000000
1	0	1.427729	2.122460	0.000000
1	0	2.082047	0.733604	0.882554
1	0	2.082047	0.733604	–0.882554

Compound **18**: *n*-PrOMe
Symmetry C_s
energy E_h = –233.7493305 au
Standard orientation

8	0	–1.268169	–0.296782	0.000000
6	0	–2.340439	0.617381	0.000000
1	0	–3.262247	0.039445	0.000000
1	0	–2.322106	1.258792	0.889715
1	0	–2.322106	1.258792	–0.889715
6	0	0.000000	0.330438	0.000000
1	0	0.097394	0.975992	0.885028
1	0	0.097394	0.975992	–0.885028
6	0	1.084938	–0.731404	0.000000
1	0	0.948184	–1.368701	–0.875927
1	0	0.948184	–1.368701	0.875927
6	0	2.488918	–0.128785	0.000000
1	0	2.655707	0.493464	0.881300
1	0	3.248739	–0.910066	0.000000
1	0	2.655707	0.493464	–0.881300

Compound **19**: *n*-BuOMe
Symmetry C_s
energy E_h = –273.0763728 au
Standard orientation

8	0	1.407588	–1.225473	0.000000
6	0	1.557704	–2.626451	0.000000

1	0	2.624521	–2.840286	0.000000
1	0	1.103722	–3.079928	0.889749
1	0	1.103722	–3.079928	–0.889749
6	0	0.055207	–0.808302	0.000000
1	0	–0.458874	–1.210170	0.884950
1	0	–0.458874	–1.210170	–0.884950
6	0	0.000000	0.708738	0.000000
1	0	0.538279	1.078100	–0.876436
1	0	0.538279	1.078100	0.876436
6	0	–1.430246	1.250736	0.000000
1	0	–1.964542	0.868329	0.874580
1	0	–1.964542	0.868329	–0.874580
6	0	–1.486850	2.777754	0.000000
1	0	–2.516310	3.137547	0.000000
1	0	–0.990489	3.189504	0.880601
1	0	–0.990489	3.189504	–0.880601

Compound **20**: Et_2O
Symmetry C_{2v}
energy E_h = −233.7548183 au
Standard orientation

8	0	0.000000	0.000000	0.257696
6	0	0.000000	1.184327	–0.517210
1	0	0.884346	1.202715	–1.168853
1	0	–0.884346	1.202715	–1.168853
6	0	0.000000	2.380714	0.412255
1	0	0.883336	2.371435	1.050344
1	0	0.000000	3.306575	–0.164040
1	0	–0.883336	2.371435	1.050344
6	0	0.000000	–1.184327	–0.517210
1	0	0.884346	–1.202715	–1.168853
1	0	–0.884346	–1.202715	–1.168853
6	0	0.000000	–2.380714	0.412255
1	0	–0.883336	–2.371435	1.050344
1	0	0.000000	–3.306575	–0.164040
1	0	0.883336	–2.371435	1.050344

Compound **21**: *i*-Pr_2O
Symmetry C_2
energy E_h = −312.4138217 au
Standard orientation

8	0	0.000000	0.000000	0.528322
6	0	0.326453	1.168936	–0.224643
1	0	–0.303711	1.207389	–1.121468
6	0	0.000000	2.368551	0.651896
1	0	0.583000	2.329958	1.573019
1	0	0.234209	3.299726	0.134901
1	0	–1.056302	2.373405	0.917682

6	0	1.793300	1.149951	–0.651334
1	0	2.023172	0.268283	–1.249819
1	0	2.031751	2.030169	–1.250561
1	0	2.439357	1.143670	0.227442
6	0	–0.326453	–1.168936	–0.224643
1	0	0.303711	–1.207389	–1.121468
6	0	0.000000	–2.368551	0.651896
1	0	–0.234209	–3.299726	0.134901
1	0	1.056302	–2.373405	0.917682
1	0	–0.583000	–2.329958	1.573019
6	0	–1.793300	–1.149951	–0.651334
1	0	–2.031751	–2.030169	–1.250561
1	0	–2.439357	–1.143670	0.227442
1	0	–2.023172	–0.268283	–1.249819

Compound **22**: *t*-Bu_2O
Symmetry C_2
energy E_h = −391.0591996 au
Standard orientation

8	0	0.000000	0.000000	0.688010
6	0	0.000000	1.296409	0.055361
6	0	–0.408591	2.225672	1.204409
1	0	0.290558	2.125193	2.033824
1	0	–0.415128	3.265881	0.877830
1	0	–1.403142	1.965331	1.564955
6	0	1.409911	1.682863	–0.420198
1	0	1.718712	1.125747	–1.301294
1	0	1.440518	2.743813	–0.672921
1	0	2.132071	1.500920	0.375271
6	0	–1.010292	1.441093	–1.089155
1	0	–2.014958	1.183206	–0.757551
1	0	–1.022752	2.478273	–1.426469
1	0	–0.756260	0.822754	–1.948189
6	0	0.000000	–1.296409	0.055361
6	0	1.010292	–1.441093	–1.089155
1	0	0.756260	–0.822754	–1.948189
1	0	2.014958	–1.183206	–0.757551
1	0	1.022752	–2.478273	–1.426469
6	0	0.408591	–2.225672	1.204409
1	0	–0.290558	–2.125193	2.033824
1	0	0.415128	–3.265881	0.877830
1	0	1.403142	–1.965331	1.564955
6	0	–1.409911	–1.682863	–0.420198
1	0	–2.132071	–1.500920	0.375271
1	0	–1.718712	–1.125747	–1.301294
1	0	–1.440518	–2.743813	–0.672921

Compound **23**: *n*-Pr_2O

Symmetry C_{2v}
energy E_h = −312.4085735 au
Standard orientation

8	0	0.000000	0.000000	0.382795
6	0	0.000000	1.183942	–0.390735
1	0	0.884778	1.205593	–1.043307
1	0	–0.884778	1.205593	–1.043307
6	0	0.000000	2.388173	0.534454
1	0	0.875861	2.328776	1.183697
1	0	–0.875861	2.328776	1.183697
6	0	0.000000	3.710182	–0.231494
1	0	0.000000	4.558092	0.453257
1	0	0.881269	3.801351	–0.869285
1	0	–0.881269	3.801351	–0.869285
6	0	0.000000	–1.183942	–0.390735
1	0	0.884778	–1.205593	–1.043307
1	0	–0.884778	–1.205593	–1.043307
6	0	0.000000	–2.388173	0.534454
1	0	–0.875861	–2.328776	1.183697
1	0	0.875861	–2.328776	1.183697
6	0	0.000000	–3.710182	–0.231494
1	0	0.881269	–3.801351	–0.869285
1	0	0.000000	–4.558092	0.453257
1	0	–0.881269	–3.801351	–0.869285

Compound **24**: *n*-Bu_2O
Symmetry C_{2v}
energy E_h = −391.0626456 au
Standard orientation

8	0	0.000000	0.000000	0.202883
6	0	0.000000	1.183918	–0.571524
1	0	0.884677	1.204019	–1.224035
1	0	–0.884677	1.204019	–1.224035
6	0	0.000000	2.388071	0.353657
1	0	0.876393	2.329857	1.004008
1	0	–0.876393	2.329857	1.004008
6	0	0.000000	3.717271	–0.402583
1	0	0.874520	3.762942	–1.058169
1	0	–0.874520	3.762942	–1.058169
6	0	0.000000	4.930249	0.526829
1	0	0.000000	5.863692	–0.037086
1	0	–0.880595	4.931425	1.171836
1	0	0.880595	4.931425	1.171836
6	0	0.000000	–1.183918	–0.571524
1	0	0.884677	–1.204019	–1.224035
1	0	–0.884677	–1.204019	–1.224035
6	0	0.000000	–2.388071	0.353657
1	0	–0.876393	–2.329857	1.004008
1	0	0.876393	–2.329857	1.004008

6	0	0.000000	–3.717271	–0.402583
1	0	0.874520	–3.762942	–1.058169
1	0	–0.874520	–3.762942	–1.058169
6	0	0.000000	–4.930249	0.526829
1	0	–0.880595	–4.931425	1.171836
1	0	0.000000	–5.863692	–0.037086
1	0	0.880595	–4.931425	1.171836

Compound **25**: H_3O^+
Symmetry C_{3v}
energy E_h = −76.7368005 au
Standard orientation

8	0	0.000000	0.000000	0.073711
1	0	0.000000	0.941788	–0.196563
1	0	0.815612	–0.470894	–0.196563
1	0	–0.815612	–0.470894	–0.196563

Compound **26**: MeH_2O^+
Symmetry C_s
energy E_h = −116.0719713 au
Standard orientation

8	0	0.037502	–0.723242	0.000000
1	0	–0.346267	–1.128173	0.799043
1	0	–0.346267	–1.128173	–0.799043
6	0	0.037502	0.795940	0.000000
1	0	0.580072	1.066423	–0.897721
1	0	–0.992639	1.133798	0.000000
1	0	0.580072	1.066423	0.897721

Compound **27**: EtH_2O^+
Symmetry C_1
energy E_h = −155.4143170 au
Standard orientation

8	0	1.195796	–0.279004	–0.090345
1	0	2.039250	0.204746	–0.036005
1	0	1.206960	–1.032973	0.526161
6	0	–0.079117	0.620156	0.050042
1	0	0.047782	1.137995	0.996016
1	0	0.038008	1.287803	–0.797137
6	0	–1.271880	–0.276838	–0.025195
1	0	–2.154449	0.362851	0.045406
1	0	–1.320436	–0.812216	–0.971082
1	0	–1.317503	–0.976081	0.810318

Compound **28**: Me_3O^+
Symmetry C_{3v}

energy E_h = −194.7294900 au

Standard orientation

8	0	0.000000	0.000000	0.296109
6	0	0.000000	1.434246	–0.065850
1	0	–0.893098	1.859177	0.377617
1	0	0.893098	1.859177	0.377617
1	0	0.000000	1.524257	–1.149756
6	0	1.242093	–0.717123	–0.065850
1	0	1.163545	–1.703034	0.377617
1	0	1.320045	–0.762128	–1.149756
1	0	2.056643	–0.156143	0.377617
6	0	–1.242093	–0.717123	–0.065850
1	0	–1.320045	–0.762128	–1.149756
1	0	–1.163545	–1.703034	0.377617
1	0	–2.056643	–0.156143	0.377617

Compound **29**: Et_3O^+

Symmetry C_3

energy E_h = −312.7361442 au

Standard orientation

8	0	0.000000	0.000000	0.143044
6	0	–1.390071	–0.451164	0.503750
1	0	–1.323216	–0.861699	1.509957
1	0	–1.971682	0.463877	0.524379
6	0	1.085755	–0.978255	0.503750
1	0	1.407861	–0.715089	1.509957
1	0	0.584112	–1.939465	0.524379
6	0	0.304316	1.429419	0.503750
1	0	–0.084645	1.576788	1.509957
1	0	1.387570	1.475588	0.524379
6	0	–0.278931	2.364674	–0.521190
1	0	0.000000	3.380890	–0.239439
1	0	0.122711	2.165417	–1.512563
1	0	–1.365994	2.326394	–0.559143
6	0	–1.908402	–1.423898	–0.521190
1	0	–2.927936	–1.690445	–0.239439
1	0	–1.936662	–0.976437	–1.512563
1	0	–1.331719	–2.346182	–0.559143
6	0	2.187333	–0.940776	–0.521190
1	0	2.927936	–1.690445	–0.239439
1	0	1.813950	–1.188980	–1.512563
1	0	2.697713	0.019788	–0.559143

Compound **30**: OH^+

Symmetry $C_{\infty v}$

energy E_h = −75.1684563 au

Standard orientation

8	0	0.000000	0.000000	0.115339

1	0	0.000000	0.000000	–0.922710

Compound **31**: H_2C=CHOH
Symmetry C_s
energy E_h = −153.8762181 au
Standard orientation

8	0	–1.100609	–0.395583	0.000000
1	0	–1.899719	0.135391	0.000000
6	0	0.000000	0.413281	0.000000
1	0	–0.201645	1.478872	0.000000
6	0	1.234430	–0.068097	0.000000
1	0	1.427263	–1.131309	0.000000
1	0	2.072388	0.610603	0.000000

Compound **32**: H_2C=CHOMe
Symmetry C_s
energy E_h = −193.1900544 au
Standard orientation

8	0	0.000000	0.668177	0.000000
6	0	–1.364344	1.061633	0.000000
1	0	–1.880096	0.696690	0.892055
1	0	–1.376215	2.147957	0.000000
1	0	–1.880096	0.696690	–0.892055
6	0	0.228836	–0.669122	0.000000
1	0	–0.660325	–1.293239	0.000000
6	0	1.450582	–1.187764	0.000000
1	0	2.332007	–0.563007	0.000000
1	0	1.574282	–2.258983	0.000000

Compound **33**: PhOH
Symmetry C_s
energy E_h = −307.5829283 au
Standard orientation

8	0	0.047984	2.302030	0.000000
6	0	0.021631	–1.851025	0.000000
6	0	–1.183473	–1.159574	0.000000
6	0	–1.200396	0.230572	0.000000
6	0	0.000000	0.936403	0.000000
6	0	1.212675	0.251937	0.000000
6	0	1.215737	–1.135690	0.000000
1	0	0.031424	–2.931808	0.000000
1	0	–2.120198	–1.700802	0.000000
1	0	–2.142818	0.765700	0.000000
1	0	2.134206	0.816857	0.000000
1	0	2.160836	–1.662262	0.000000
1	0	–0.844358	2.660331	0.000000

Compound **34**: $H_2C{=}O$
Symmetry C_{2v}
energy E_h = −114.5499452 au
Standard orientation

8	0	0.000000	0.000000	0.672428
6	0	0.000000	0.000000	–0.526024
1	0	0.000000	0.938212	–1.111639
1	0	0.000000	–0.938212	–1.111639

Compound **35**: H(HO)C=O∗, **36**: H(HO∗)C=O
Symmetry C_s
energy E_h = −189.8416527 au
Standard orientation

8	0	1.157012	0.116930	0.000000
6	0	0.000000	0.420408	0.000000
1	0	–0.382893	1.447570	0.000000
8	0	–1.026765	–0.445362	0.000000
1	0	–0.659085	–1.342561	0.000000

Compound **18**$_{gauche}$: *n*-PrOMe
Symmetry C_1
energy E_h = −233.7493287 au
Standard orientation

8	0	0.899488	–0.291521	–0.354237
6	0	2.243423	–0.272821	0.067292
1	0	2.763865	–1.067312	–0.463575
1	0	2.724440	0.685309	–0.165329
1	0	2.328841	–0.450031	1.146445
6	0	0.105472	0.704008	0.265146
1	0	0.515500	1.697908	0.039380
1	0	0.136182	0.576044	1.357292
6	0	–1.323808	0.597678	–0.238369
1	0	–1.884318	1.441967	0.171420
1	0	–1.318356	0.721522	–1.323740
6	0	–2.009442	–0.715639	0.135094
1	0	–3.032078	–0.743779	–0.242352
1	0	–1.472157	–1.567188	–0.279670
1	0	–2.051688	–0.841632	1.219047

Compound **19**$_{gauche}$: *n*-BuOMe
Symmetry C_1
energy E_h = −273.0764793 au
Standard orientation

8	0	1.442030	–0.355237	–0.334214
6	0	2.800518	–0.449007	0.026261
1	0	3.367241	0.428185	–0.309628
1	0	2.922768	–0.545212	1.112110
1	0	3.205956	–1.336760	–0.454824

6	0	0.791766	0.771347	0.226425
1	0	1.293570	1.690489	–0.105628
1	0	0.867135	0.734736	1.323157
6	0	–0.664988	0.782901	–0.203411
1	0	–0.705199	0.802373	–1.295924
1	0	–1.109146	1.720860	0.143540
6	0	–1.479713	–0.398924	0.324116
1	0	–1.019936	–1.328165	–0.015262
1	0	–1.426925	–0.409430	1.417154
6	0	–2.942360	–0.354486	–0.115057
1	0	–3.500875	–1.205497	0.276444
1	0	–3.027427	–0.375634	–1.203335
1	0	–3.434740	0.554963	0.235907

Compound **23**$_{\text{gauche}}$: *n*-Pr_2O
Symmetry C_2
energy E_h = −312.4084607 au
Standard orientation

8	0	0.000000	0.000000	0.115698
6	0	0.004110	1.184394	0.889992
1	0	–0.878534	1.202335	1.546238
1	0	0.892512	1.202532	1.535873
6	0	0.000000	2.393647	–0.030139
1	0	0.112049	3.285376	0.592154
1	0	0.883779	2.344958	–0.670528
6	0	–1.260431	2.509403	–0.885942
1	0	–1.221491	3.394117	–1.522291
1	0	–1.377922	1.636779	–1.526773
1	0	–2.152484	2.588528	–0.260925
6	0	–0.004110	–1.184394	0.889992
1	0	0.878534	–1.202335	1.546238
1	0	–0.892512	–1.202532	1.535873
6	0	0.000000	–2.393647	–0.030139
1	0	–0.112049	–3.285376	0.592154
1	0	–0.883779	–2.344958	–0.670528
6	0	1.260431	–2.509403	–0.885942
1	0	1.221491	–3.394117	–1.522291
1	0	1.377922	–1.636779	–1.526773
1	0	2.152484	–2.588528	–0.260925

Compound **24**$_{\text{gauche}}$: *n*-Bu_2O
Symmetry C_2
energy E_h = −391.0627692 au
Standard orientation

8	0	0.000000	0.000000	0.523702
6	0	–0.000314	1.184073	1.299203
1	0	–0.886154	1.201441	1.948577
1	0	0.884242	1.200000	1.952763

6	0	0.000000	2.395058	0.381983
1	0	–0.880863	2.343800	–0.263911
1	0	–0.119869	3.286806	1.004819
6	0	1.261232	2.531044	–0.472603
1	0	1.380937	1.630951	–1.077327
1	0	2.134419	2.579016	0.185320
6	0	1.235587	3.762066	–1.376967
1	0	1.142862	4.681157	–0.794422
1	0	2.146828	3.837566	–1.971490
1	0	0.391781	3.724576	–2.068830
6	0	0.000314	–1.184073	1.299203
1	0	–0.884242	–1.200000	1.952763
1	0	0.886154	–1.201441	1.948577
6	0	0.000000	–2.395058	0.381983
1	0	0.119869	–3.286806	1.004819
1	0	0.880863	–2.343800	–0.263911
6	0	–1.261232	–2.531044	–0.472603
1	0	–1.380937	–1.630951	–1.077327
1	0	–2.134419	–2.579016	0.185320
6	0	–1.235587	–3.762066	–1.376967
1	0	–1.142862	–4.681157	–0.794422
1	0	–2.146828	–3.837566	–1.971490
1	0	–0.391781	–3.724576	–2.068830

Procedure to draw the selected contributions from each ψ_i to σ^d and σ^p and each $\psi_i \rightarrow \psi_a$ transition, using molecular orbitals

(The procedure, analyzing the output of Gaussian program, with the utility program, is explained, exemplified by H_2O: The output format below is the same as that from the program.)

Output

SP: B3LYP/6-311++G(3df,3pd)

Number of Basis Functions	=	83
Number of Orbitals	=	83
Number of Atoms	=	3
Multiplicity	=	1
Number of Electrons	=	10

Diamagnetic MO contribution

1	270.61732	270.60956	270.61250
2	39.48301	37.69066	39.27237
3	21.13187	17.49616	17.92855
4	28.66156	30.44936	22.94863
5	22.33530	44.37664	44.94523
SUM	382.22906	400.62238	395.70728

Paramagnetic MO contribution

OCC x OCC	148.97707	77.28316	101.64450
1	-0.00111	-0.00103	0.00001
2	-10.27629	-5.57952	0.15029
3	-87.09246	-0.20783	-63.38689
4	-134.64642	-36.35417	-0.01775
5	-0.02095	-72.96107	-117.66898
SUM	-83.06016	-37.82046	-79.27883

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Appendix

Procedure to draw the selected contributions from each ψ_i to σ^d and σ^p and each $\psi_i \rightarrow \psi_a$ transition, using molecular orbitals

(The procedure, analyzing the output of Gaussian program, with the utility program, is explained, exemplified by H_2O: The output format below is the same as that from the program.)

Output

SP: B3LYP/6-311++G(3df,3pd)
 Number of Basis Functions = 83
 Number of Orbitals = 83
 Number of Atoms = 3
 Multiplicity = 1
 Number of Electrons = 10

Diamagnetic MO contribution

1	270.61732	270.60956	270.61250
2	39.48301	37.69066	39.27237
3	21.13187	17.49616	17.92855
4	28.66156	30.44936	22.94863
5	22.33530	44.37664	44.94523
SUM	382.22906	400.62238	395.70728

Paramagnetic MO contribution

OCC-->OCC	148.97707	77.28316	101.64450
--			
1--> 6	0.00000	0.00000	0.00000
1--> 7	0.00007	0.00000	0.00000
1--> 8	0.00000	0.00000	0.00000
1--> 9	0.00015	0.00000	0.00000
1--> 10	0.00000	0.00000	0.00000
1--> 11	0.00000	-0.00017	0.00000
1--> 12	0.00000	0.00000	0.00000
1--> 13	-0.00035	0.00000	0.00000
1--> 14	0.00000	0.00000	0.00000
1--> 15	0.00000	0.00000	0.00000
1--> 16	0.00000	-0.00009	0.00000
1--> 17	0.00017	0.00000	0.00000
1--> 18	0.00000	0.00000	0.00000
1--> 19	-0.00003	0.00000	0.00000
1--> 20	0.00000	0.00000	0.00000
1--> 21	0.00007	0.00000	0.00000
1--> 22	0.00000	0.00000	0.00000
1--> 23	0.00000	0.00013	0.00000
1--> 24	0.00000	0.00000	0.00000
1--> 25	0.00000	0.00000	0.00001
1--> 26	-0.00013	0.00000	0.00000
1--> 27	0.00000	0.00000	0.00000
1--> 28	0.00000	-0.00042	0.00000

1--> 29	0.00000	0.00000	0.00000
1--> 30	-0.00006	0.00000	0.00000
---		-- omitted --	---
1--> 83	0.00000	0.00000	0.00000

--

2--> 6	0.00000	0.00000	0.00000
2--> 7	-0.46140	0.00000	0.00000
2--> 8	0.00000	0.00000	0.00000
2--> 9	-1.54627	0.00000	0.00000
2--> 10	0.00000	0.00000	0.00000
2--> 11	0.00000	-1.31063	0.00000
2--> 12	0.00000	0.00000	0.00000
2--> 13	-1.56968	0.00000	0.00000
2--> 14	0.00000	0.00000	0.00000
2--> 15	0.00000	0.00000	0.04059
2--> 16	0.00000	-0.46515	0.00000
2--> 17	-0.73001	0.00000	0.00000
2--> 18	0.00000	0.00000	0.00000
2--> 19	-0.74776	0.00000	0.00000
2--> 20	0.00000	0.00000	0.00000
2--> 21	-1.20339	0.00000	0.00000
2--> 22	0.00000	0.00000	0.00000
2--> 23	0.00000	-0.63944	0.00000
2--> 24	0.00000	0.00000	0.00000
2--> 25	0.00000	0.00000	0.04077
2--> 26	-1.20559	0.00000	0.00000
2--> 27	0.00000	0.00000	0.00000
2--> 28	0.00000	-1.90971	0.00000
2--> 29	0.00000	0.00000	0.00000
2--> 30	-0.35428	0.00000	0.00000
---		-- omitted --	---
2--> 83	0.00000	0.00000	0.00000

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3--> 6	-16.10823	0.00000	0.00000
3--> 7	0.00000	0.00000	0.00000
3--> 8	-28.12427	0.00000	0.00000
3--> 9	0.00000	0.00000	0.00000
3--> 10	-8.79592	0.00000	0.00000
3--> 11	0.00000	0.00000	-32.21992
3--> 12	-0.54182	0.00000	0.00000
3--> 13	0.00000	0.00000	0.00000
3--> 14	1.23338	0.00000	0.00000
3--> 15	0.00000	-0.05070	0.00000
3--> 16	0.00000	0.00000	-3.05255
3--> 17	0.00000	0.00000	0.00000
3--> 18	-9.64160	0.00000	0.00000
3--> 19	0.00000	0.00000	0.00000
3--> 20	-3.65496	0.00000	0.00000
3--> 21	0.00000	0.00000	0.00000
3--> 22	0.29175	0.00000	0.00000
3--> 23	0.00000	0.00000	-8.22945
3--> 24	-13.26418	0.00000	0.00000
3--> 25	0.00000	-0.11824	0.00000
3--> 26	0.00000	0.00000	0.00000
3--> 27	0.70959	0.00000	0.00000
3--> 28	0.00000	0.00000	-10.50555
3--> 29	-0.35559	0.00000	0.00000
3--> 30	0.00000	0.00000	0.00000
---		-- omitted --	---

3--> 83	0.00060	0.00000	0.00000
--			
4--> 6	0.00000	0.00000	0.00000
4--> 7	-10.93409	0.00000	0.00000
4--> 8	0.00000	0.00000	0.00000
4--> 9	-40.87481	0.00000	0.00000
4--> 10	0.00000	0.00000	0.00000
4--> 11	0.00000	-21.08688	0.00000
4--> 12	0.00000	0.00000	0.00000
4--> 13	-18.68673	0.00000	0.00000
4--> 14	0.00000	0.00000	0.00000
4--> 15	0.00000	0.00000	-0.02769
4--> 16	0.00000	1.05262	0.00000
4--> 17	-25.64554	0.00000	0.00000
4--> 18	0.00000	0.00000	0.00000
4--> 19	-5.33603	0.00000	0.00000
4--> 20	0.00000	0.00000	0.00000
4--> 21	-14.99557	0.00000	0.00000
4--> 22	0.00000	0.00000	0.00000
4--> 23	0.00000	-6.00917	0.00000
4--> 24	0.00000	0.00000	0.00000
4--> 25	0.00000	0.00000	-0.03728
4--> 26	-0.38139	0.00000	0.00000
4--> 27	0.00000	0.00000	0.00000
4--> 28	0.00000	-5.21634	0.00000
4--> 29	0.00000	0.00000	0.00000
4--> 30	-0.93718	0.00000	0.00000
---		-- omitted --	---
4--> 83	0.00000	0.00000	0.00000
--			
5--> 6	0.00000	-23.26956	0.00000
5--> 7	0.00000	0.00000	7.62655
5--> 8	0.00000	-33.36702	0.00000
5--> 9	0.00000	0.00000	-58.81056
5--> 10	0.00000	12.07783	0.00000
5--> 11	0.00000	0.00000	0.00000
5--> 12	0.00000	0.35204	0.00000
5--> 13	0.00000	0.00000	-10.27637
5--> 14	0.00000	3.07579	0.00000
5--> 15	-0.01244	0.00000	0.00000
5--> 16	0.00000	0.00000	0.00000
5--> 17	0.00000	0.00000	-32.48933
5--> 18	0.00000	-18.90842	0.00000
5--> 19	0.00000	0.00000	-2.14260
5--> 20	0.00000	-5.97271	0.00000
5--> 21	0.00000	0.00000	-18.68527
5--> 22	0.00000	0.15550	0.00000
5--> 23	0.00000	0.00000	0.00000
5--> 24	0.00000	-2.61514	0.00000
5--> 25	-0.00193	0.00000	0.00000
5--> 26	0.00000	0.00000	7.18480
5--> 27	0.00000	-0.28825	0.00000
5--> 28	0.00000	0.00000	0.00000
5--> 29	0.00000	1.04724	0.00000
5--> 30	0.00000	0.00000	2.80524
---		-- omitted --	---
5--> 83	0.00000	-0.00002	0.00000
SUM	-83.06016	-37.82046	-79.27883

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Drawing steps:

1. Selecting transitions in the above output terms, of which contributions are larger than a certain value.
2. Drawing the molecular orbitals in the selected transitions using GaussView.
3. Completing the transition maps of interest, using the molecular orbitals drawn above.
   (See Figs. 6–12 in the text.)