Spectroscopic Characterization of Silica Aerogels Prepared Using Several Precursors - Effect on the Formation of Molecular Clusters

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† Electronic Supplementary Information (ESI)

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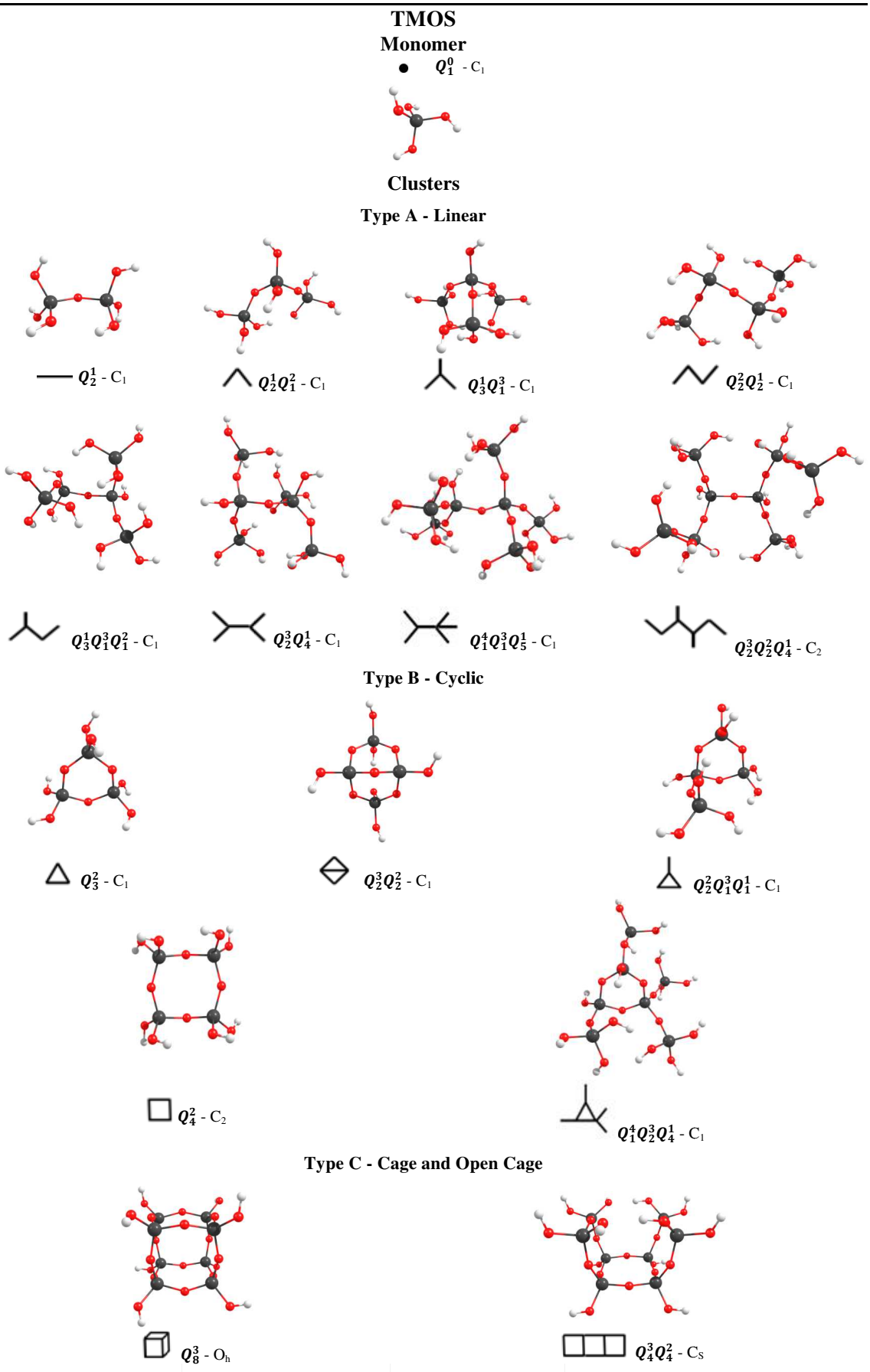

Fig. S-1 - B3LYP/6-311+G(d,p) optimized structures of the **TMOS** based clusters, including a schematic representation. The symmetry point groups of the most stable conformers are also showed. Q_n^m, where n represents the number of silicons that are bonded to m bridging oxygens, according to reference.[32]

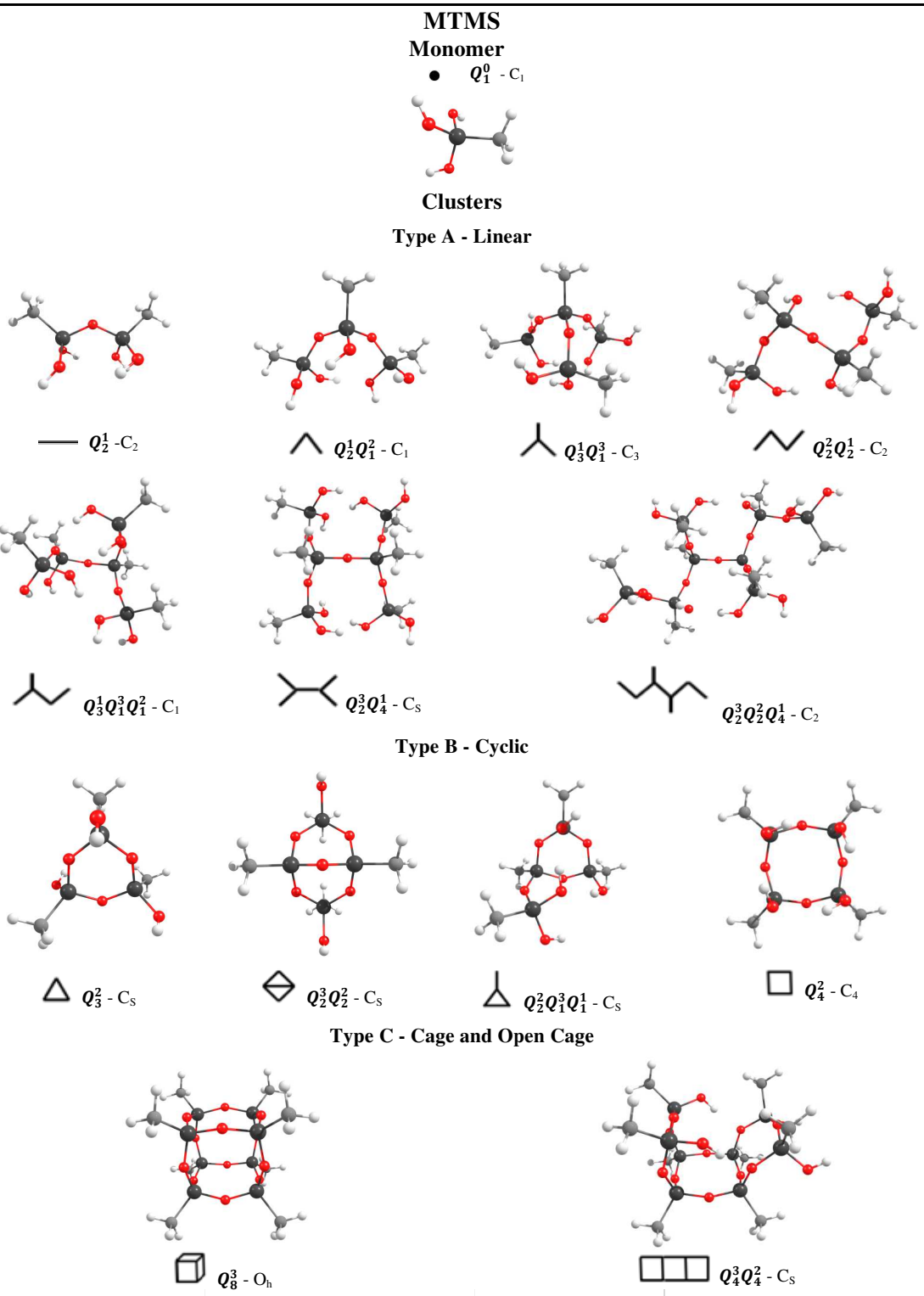

Fig. S-2 - B3LYP/6-311+G(d,p) optimized structures of the **MTMS** based clusters, including a schematic representation. The symmetry point groups of the most stable conformers are also showed. Q_n^m, where *n* represents the number of silicons that are bonded to *m* bridging oxygens, according to to reference.[32]

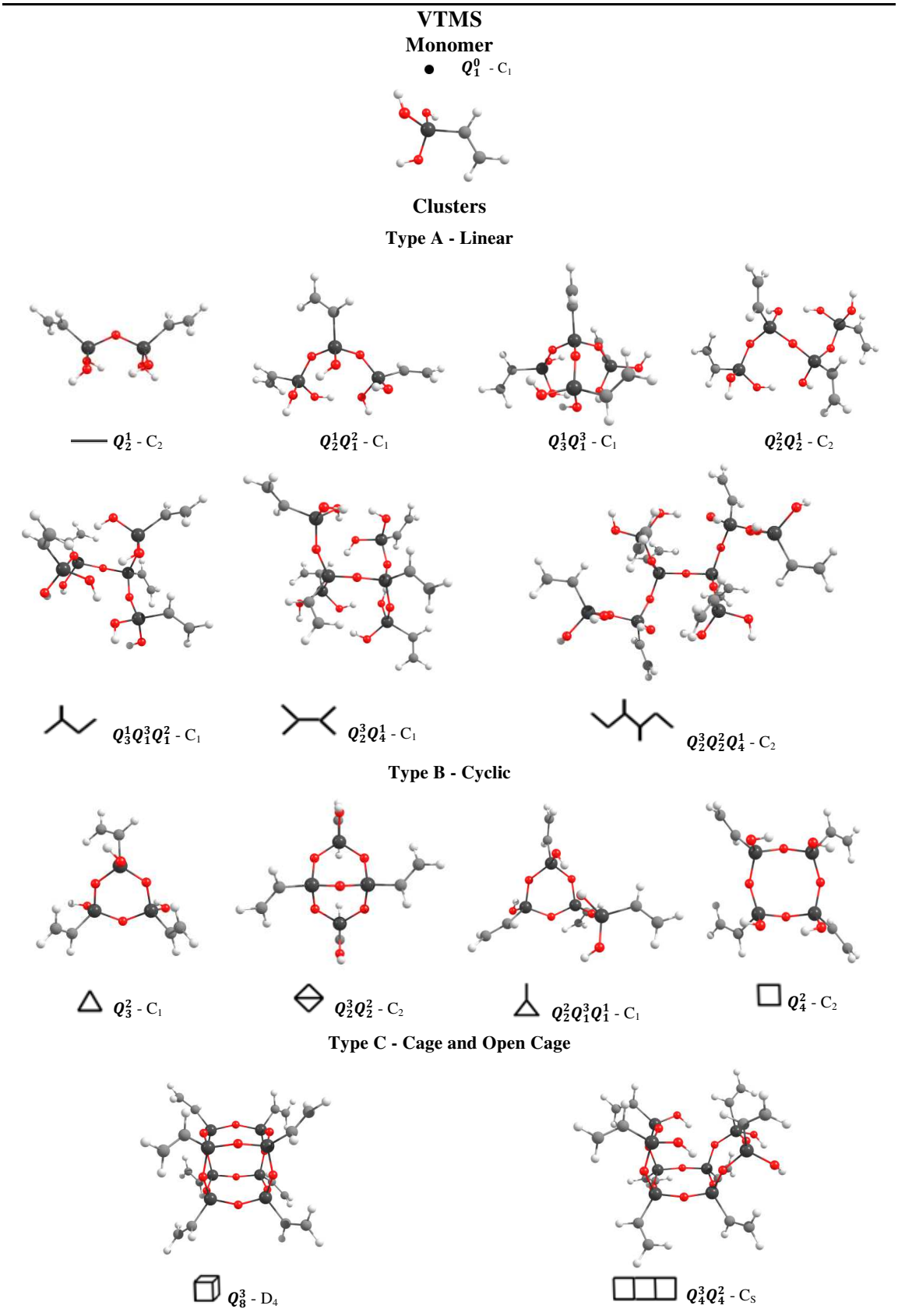

Fig. S-3 - B3LYP/6-311+G(d,p) optimized structures of the **VTMS** based clusters, including a schematic representation. The symmetry point groups of the most stable conformers are also showed. Q_n^m, where n represents the number of silicons that are bonded to m bridging oxygens, according to reference.[32]

Table S-1: Calculated [B3LYP/IGLO-III] chemical shifts relative to TMS for all species considered in this study.

		Precursors					
		TMOS		MTMS		VTMS	
		Silicon environments	*δ (ppm)[a]*	*Silicon environments*	*δ (ppm)[a]*	*Silicon environments*	*δ (ppm)[a]*
Monomer							
●	Q_1^0	Q0	-81.06	T0	-40.56	T0	-59.43
Cluster							
Type A - Linear							
—	Q_2^1	Q1	-90.96	T1	-47.07	T1	-71.93
		Q1	-88.50	T1	-44.93	T1	-72.11
∧	$Q_2^1Q_1^2$	Q2	-99.12	T2	-50.04	T2	-81.11
		Q1	-94.66	T1	-45.41	T1	-67.40
		Q1	-88.83	T1	-43.39	T1	-67.02
Y	$Q_3^1Q_1^3$	Q3	-111.24	T3	-72.49	T3	-88.39
		Q1	-94.09	T1	-49.41	T1	-67.31
		Q1	-90.17	T1	-49.39	T1	-66.85
		Q1	-88.00	T1	-49.34	T1	-66.79
∧∧	$Q_2^2Q_2^1$	Q2	-104.46	T2	-64.38	T2	-78.06
		Q2	-98.80	T2	-64.38	T2	-78.06
		Q1	-92.51	T1	-53.62	T1	-66.38
		Q1	-88.59	T1	-53.62	T1	-66.38
⅄	$Q_3^1Q_1^3Q_1^2$	Q3	-115.82	T3	-78.73	T3	-93.16
		Q2	-101.29	T2	-57.82	T2	-74.95
		Q1	-91.85	T1	-51.55	T1	-70.08
		Q1	-90.22	T1	-50.44	T1	-69.01
		Q1	-87.98	T1	-43.65	T1	-63.78
X	$Q_2^3Q_4^1$	Q3	-121.65	T3	-83.79	T3	-100.60
		Q3	-118.02	T3	-81.92	T3	-96.41
		Q1	-96.74	T1	-55.95	T1	-73.97
		Q1	-94.54	T1	-55.95	T1	-73.09
		Q1	-93.05	T1	-51.44	T1	-68.81
		Q1	-91.43	T1	-51.44	T1	-68.43
⋋	$Q_1^4Q_1^3Q_5^1$	Q4	-128.74	-	-	-	-
		Q3	-114.25	-	-	-	-
		Q1	-97.97	-	-	-	-
		Q1	-95.06	-	-	-	-
		Q1	-94.03	-	-	-	-
		Q1	-93.61	-	-	-	-
		Q1	-88.39	-	-	-	-
⋔	$Q_2^3Q_2^2Q_4^1$	Q3	-119.38	T3	-77.24	T3	-91.92
		Q3	-119.38	T3	-77.24	T3	-91.92
		Q2	-103.78	T2	-59.47	T2	-77.48
		Q2	-103.78	T2	-59.47	T2	-77.48
		Q1	-93.97	T1	-53.73	T1	-70.35
		Q1	-93.97	T1	-53.73	T1	-70.35
		Q1	-93.27	T1	-47.15	T1	-64.94
		Q1	-93.27	T1	-47.15	T1	-64.94
Type B - Cyclic							
△	Q_3^2	Q2	-96.86	T2	-57.02	T2	-75.23
		Q2	-96.86	T2	-57.02	T2	-73.75
		Q2	-96.05	T2	-56.28	T2	-73.75
◇	$Q_2^3Q_2^2$	Q3	-96.36	T2	-53.23	T2	-71.96
		Q3	-95.81	T2	-53.23	T2	-71.96
		Q2	-94.23	T3	-50.68	T3	-69.07
		Q2	-93.65	T3	-50.68	T3	-69.07

	$Q_2^2Q_1^3Q_1^1$	Q3	-104.87	T3	-65.00	T3	-82.04
		Q2	-95.30	T2	-55.77	T2	-74.03
		Q2	-94.00	T2	-52.80	T2	-71.52
		Q1	-91.72	T1	-51.27	T1	-70.57
	Q_4^2	Q2	-101.98	T2	-51.55	T2	-75.86
		Q2	-101.98	T2	-51.55	T2	-75.86
		Q2	-99.67	T2	-51.55	T2	-74.42
		Q2	-99.67	T2	-51.55	T2	-74.42
	$Q_1^4Q_2^3Q_4^1$	Q4	-121.61	-	-	-	-
		Q3	-104.80	-	-	-	-
		Q3	-104.77	-	-	-	-
		Q1	-95.01	-	-	-	-
		Q1	-93.47	-	-	-	-
		Q1	-90.30	-	-	-	-
		Q1	-89.99	-	-	-	-
Type C - Cage and Open Cage							
	Q_8^3	Q3	-115.93	T3	-77.02	T3	-93.46
		Q3	-115.93	T3	-77.02	T3	-93.46
		Q3	-115.93	T3	-77.02	T3	-93.46
		Q3	-115.93	T3	-77.02	T3	-93.46
		Q3	-115.81	T3	-77.02	T3	-93.46
		Q3	-115.81	T3	-77.02	T3	-93.46
		Q3	-115.81	T3	-77.02	T3	-93.46
		Q3	-115.81	T3	-77.02	T3	-93.46
	$Q_4^3Q_4^2$	Q3	-118.75	T3	-75.30	T3	-90.20
		Q3	-118.75	T3	-75.30	T3	-90.20
		Q3	-118.31	T3	-71.53	T3	-89.73
		Q3	-118.31	T3	-71.53	T3	-89.73
		Q2	-106.59	T2	-65.53	T2	-79.74
		Q2	-106.04	T2	-65.53	T2	-79.74
		Q2	-106.04	T2	-58.66	T2	-77.93
		Q2	-106.59	T2	-58.66	T2	-77.93

[a] Relative to the calculated [B3LYP/IGLO-III] chemical shifts of the TMS molecule; δ_{TMS} = 330.23 ppm.