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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

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		Precursors							
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			TMOS MTMS			VTN	VTMS		
Monomer Constraints 11			Silicon	$\delta (ppm)^a$	Silicon	$\delta (ppm)^a$	Silicon	$\delta (ppm)^a$	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Monomer		environments	 ,	environments	41 ×	environments	u <i>i i</i>	
Cluster 10 40.0 10 40.0 10 59.43 Type A - Linear T 47.07 T 71.93 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.1 71.93 71.7 71.93 71.93 71.93 71.93<		00	00	<u> 91.06</u>	TO	40.56	TO	50.42	
Cunser Type A - Linear \sim $Q_2^{\frac{1}{2}}Q_1^2$ Q_1 -90.96 T1 -47.07 T1 -71.93 \wedge $Q_2^{\frac{1}{2}}Q_1^2$ Q_2 -99.12 T2 -50.04 T1 -47.07 \wedge $Q_2^{\frac{1}{2}}Q_1^2$ Q_2 -99.12 T2 -50.04 T1 -67.02 \downarrow $Q_2^{\frac{1}{2}}Q_1^{\frac{1}{2}}$ $Q_3^{\frac{1}{2}}$	Classferr	Q_1	Qu	-81.00	10	-40.30	10	-39.43	
Type A - Linear Q1 -90.96 T1 -47.07 T1 -71.93 \wedge Q_2^2 Q_1^2 Q2 -90.12 T2 -50.04 T2 -81.11 \wedge Q_2^2 Q_1^2 Q2 -90.12 T2 -50.04 T2 -81.11 \wedge Q_2^2 Q_1^2 Q2 -90.12 T2 -50.04 T1 -67.40 \downarrow Q_3Q_1^2 Q3 -111.24 T3 -72.49 T3 -88.39 \vee Q_2^2Q_1^3 Q2 -104.46 T2 -64.38 T2 -78.06 \vee Q_2^2Q_1^3 Q2 -104.46 T2 -64.38 T2 -78.06 \vee Q_2^2Q_1^3 Q2 -101.29 T3 -78.73 T3 -93.16 \vee Q_2^2Q_1^2 Q3 -115.82 T1 -55.62 T1 -66.38 \vee Q_2^2Q_1^2 Q3 -15.87 T3 -39.16 T1 -71.93 $Q1 -91.83$									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Type A - Line	ear							
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		O_2^1	01	-90.96	T1	-47.07	T1	-71.93	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		€2	Q1	-88.50	T1	-44.93	T1	-72.11	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	\sim	$Q_{2}^{1}Q_{1}^{2}$	Q2	-99.12	T2	-50.04	T2	-81.11	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Q1	-94.66	T1 T1	-45.41	Tl Tl	-67.40	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			QI	-88.85	11	-43.39	11	-07.02	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Y	$0^{1}0^{3}$	03	-111 24	ТЗ	-72 49	ТЗ	-88 39	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Q_3Q_1	Q3 01	-94.09	T1	-49 41	T1	-67.31	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			01	-90.17	T1	-49.39	T1	-66.85	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Q1	-88.00	T1	-49.34	T1	-66.79	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	\sim	0201	02	104.46	TO	64.29	ΤĴ	79.06	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_{\overline{2}}Q_{\overline{2}}$	Q2 02	-104.40	12 T2	-04.38	12 T2	-78.06	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q2 01	-98.80	T2 T1	-53.62	T2 T1	-66 38	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			01	-88.59	T1	-53.62	T1	-66.38	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			C.						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	\sim	$Q_3^1 Q_1^3 Q_1^2$	Q3	-115.82	T3	-78.73	Т3	-93.16	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		05 01 01	Q2	-101.29	T2	-57.82	T2	-74.95	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Q1	-91.85	T1	-51.55	T1	-70.08	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q1	-90.22	T1	-50.44	T1	-69.01	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Q1	-87.98	T1	-43.65	T1	-63.78	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	\searrow	- 2 - 1							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		$Q_{2}^{3}Q_{4}^{1}$	Q3	-121.65	T3	-83.79	T3 T2	-100.60	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q3	-118.02	13 T1	-81.92	13 T1	-96.41	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				-90.74	11 T1	-55.95	T1	-73.09	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			01	-93.05	T1	-51 44	T1	-68.81	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			01	-91.43	T1	-51.44	T1	-68.43	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S		Č,						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	\rightarrow	$0_{1}^{4}0_{1}^{3}0_{5}^{1}$	04	-128.74	-	-	-	-	
$\oint_{Q_1^3} Q_2^2 Q_4^1 = \begin{array}{ccccccccccccccccccccccccccccccccccc$		\$1\$1\$5	03	-114.25	-	-	-	-	
$\oint Q_2^1 Q_2^2 Q_4^2 = \begin{array}{ccccccccccccccccccccccccccccccccccc$			Q1	-97.97	-	-	-	-	
$ \oint Q_2^1 Q_2^2 Q_2^2 Q_4^1 = Q_3 - 119.38 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - $			Q1	-95.06	-	-	-	-	
$ \oint Q_2^1 Q_2^2 Q_4^1 = \begin{array}{ccccccccccccccccccccccccccccccccccc$			Q1	-94.03	-	-	-	-	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q1	-93.61	-	-	-	-	
$ \oint Q_2^3 Q_2^2 Q_4^1 = \begin{array}{ccccccccccccccccccccccccccccccccccc$			QI	-88.39	-	-	-	-	
$ \begin{split} & \swarrow \qquad Q_2^3 Q_2^2 Q_4^1 & Q_3 & -119.38 & T_3 & -77.24 & T_3 & -91.92 \\ Q_3 & -119.38 & T_3 & -77.24 & T_3 & -91.92 \\ Q_2 & -103.78 & T_2 & -59.47 & T_2 & -77.48 \\ Q_2 & -103.78 & T_2 & -59.47 & T_2 & -77.48 \\ Q_1 & -93.97 & T_1 & -53.73 & T_1 & -70.35 \\ Q_1 & -93.97 & T_1 & -53.73 & T_1 & -70.35 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ Q_2 & -96.86 & T_2 & -57.02 & T_2 & -75.23 \\ Q_2 & -96.86 & T_2 & -57.02 & T_2 & -73.75 \\ Q_2 & -96.05 & T_2 & -56.28 & T_2 & -73.75 \\ & Q_2^3 & Q_2^3 & Q_2^3 & -96.36 & T_2 & -53.23 & T_2 & -71.96 \\ & Q_3^3 & -95.81 & T_2 & -53.23 & T_2 & -71.96 \\ & Q_2 & -94.23 & T_3 & -50.68 & T_3 & -69.07 \\ & Q_3 & -95.81 & T_2 & -53.23 & T_3 & -50.68 \\ & Q_3 & -95.81 & T_2 & -53.23 & T_3 & -50.68 \\ & Q_3 & -95.81 & T_3 & -50.68 & T_3 & -69.07 \\ & Q_3 & -95.81 & T_3 & -50.68 & T_3 & -69.07 \\ & Q_3 & -95.81 & T_3 & -50.68 & T_3 & -69.07 \\ & Q_3 & -95.81 & T_3 & -50.68 & T_3 & -69.0$	\checkmark								
$ \begin{split} & \begin{array}{ccccccccccccccccccccccccccccccccccc$	• 1 •	$Q_2^3 Q_2^2 Q_4^1$	Q3	-119.38	Т3	-77.24	Т3	-91.92	
$ \oint Q_2^2 -103.78 \qquad 112 \qquad -59.47 \qquad 112 \qquad -77.48 \\ Q_2 & -103.78 & T_2 & -59.47 & T_2 & -77.48 \\ Q_1 & -93.97 & T_1 & -53.73 & T_1 & -70.35 \\ Q_1 & -93.97 & T_1 & -53.73 & T_1 & -70.35 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ Q_1 & -93.27 & T_1 & -47.15 & T_1 & -64.94 \\ \hline \textbf{Type B - Cyclic} \\ \textbf{Y} \textbf{P} \textbf{B} - \textbf{Cyclic} \\ \textbf{Q}_3^2 & Q_2^2 & -96.86 & T_2 & -57.02 & T_2 & -75.23 \\ Q_2 & -96.86 & T_2 & -57.02 & T_2 & -75.23 \\ Q_2 & -96.86 & T_2 & -57.02 & T_2 & -73.75 \\ Q_2 & -96.05 & T_2 & -56.28 & T_2 & -73.75 \\ Q_2 & -96.05 & T_2 & -56.28 & T_2 & -71.96 \\ Q_3 & -95.81 & T_2 & -53.23 & T_2 & -71.96 \\ Q_2 & -94.23 & T_3 & -50.68 & T_3 & -69.07 \\ Q_2 & -93.65 & T_3 & -50.68 & T_3 & -69.07 \\ \end{pmatrix} $			Q3	-119.38	T3	-77.24	T3	-91.92	
$\oint Q_2^2 Q_2^2 Q_2^2 = \frac{-105.78}{93.97} 12 = -59.47 12 = -77.48$ $Q_1 = -93.97 T_1 = -53.73 T_1 = -70.35$ $Q_1 = -93.97 T_1 = -53.73 T_1 = -70.35$ $Q_1 = -93.27 T_1 = -47.15 T_1 = -64.94$ $Q_1 = -93.27 T_1 = -47.15 T_1 = -64.94$ $Q_1 = -93.27 T_1 = -47.15 T_1 = -64.94$ $Q_2 = -96.86 T_2 = -57.02 T_2 = -75.23$ $Q_2 = -96.86 T_2 = -57.02 T_2 = -75.23$ $Q_2 = -96.86 T_2 = -57.02 T_2 = -73.75$ $Q_2 = -96.05 T_2 = -56.28 T_2 = -73.75$ $Q_2 = -96.05 T_2 = -56.28 T_2 = -71.96$ $Q_2 = -96.36 T_2 = -53.23 T_2 = -71.96$ $Q_2 = -94.23 T_3 = -50.68 T_3 = -69.07$			Q2	-103.78	T2 T2	-59.47	12 T2	-77.48	
$\oint Q_2^1 Q_2^2 Q_2^2 Q_2^2 Q_2^3 = \frac{96.86}{22} -\frac{11}{99.377} + \frac{11}{71} -\frac{53.73}{73} + \frac{11}{71} -\frac{70.35}{70.35} + \frac{11}{71} -\frac{70.35}{70.35} + \frac{11}{71} -\frac{70.35}{70.35} + \frac{11}{71} +\frac{70.35}{71} +\frac{70.35}$			Q2 01	-105.78	12 T1	-39.47	12 T1	-77.48	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			Q1 01	-93.97	T1 T1	-53.73	T1	-70.35	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			01	-93.27	T1	-47.15	T1	-64 94	
Type B - Cyclic Δ 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 Q2 -96.36 T2 -56.28 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			01	-93.27	T1	-47.15	T1	-64.94	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Type B - Cycl	lic							
$ \Delta \qquad Q_3^2 \qquad Q_2^2 \qquad Q_2^2 \qquad -96.86 \qquad T_2^2 \qquad -57.02 \qquad T_2^2 \qquad -75.23 \\ Q_2 \qquad -96.86 \qquad T_2 \qquad -57.02 \qquad T_2 \qquad -73.75 \\ Q_2 \qquad -96.05 \qquad T_2 \qquad -56.28 \qquad T_2 \qquad -73.75 \\ \bullet \qquad Q_2^3 Q_2^2 \qquad Q_3 \qquad -96.36 \qquad T_2 \qquad -53.23 \qquad T_2 \qquad -71.96 \\ Q_3 \qquad -95.81 \qquad T_2 \qquad -53.23 \qquad T_2 \qquad -71.96 \\ Q_2 \qquad -94.23 \qquad T_3 \qquad -50.68 \qquad T_3 \qquad -69.07 \\ Q_2 \qquad -93.65 \qquad T_3 \qquad -50.68 \qquad T_3 \qquad -69.07 \\ \end{array} $		2							
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	\bigtriangleup	Q_{3}^{2}	Q2	-96.86	T2	-57.02	T2	-75.23	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q2	-96.86	T2	-57.02	T2	-73.75	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			Q2	-96.05	12	-36.28	12	-/3./3	
$\bigvee \begin{array}{cccccccccccccccccccccccccccccccccccc$	\bigtriangleup	0302	02	06.26	T 2	50.00	TO	71.07	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	\sim	$Q_2^2 Q_2^2$	Q3	-90.30 _05.91	12 T2	-35.25	12 T2	-/1.90	
Ω_2^2 -93.65 T3 -50.68 T3 -69.07			$\frac{\sqrt{3}}{02}$	-93.01	T2 T3	-55.25 -50.68	T3	-69.07	
			\tilde{Q}^{-}_{2}	-93.65	T3	-50.68	T3	-69.07	

Table S-1: Calculated [B3LYP/IGLO-III] chemical shifts relative to TMS for all species considered in this study.
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L	02 03 01	~~~	104.07		65.00	T 2	00.04
\bigtriangleup	$Q_2^2 Q_1^3 Q_1^4$	Q3	-104.87	13	-65.00	13	-82.04
		Q2	-95.30	12	-55.77	12	-74.03
		Q2	-94.00	12	-52.80	12	-71.52
		QI	-91.72	TI	-51.27	11	-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
T							
~							
	$Q_1^4 Q_2^3 Q_4^1$	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	<u>!</u>					
	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	Т3	-77.02	T3	-93.46
	$Q_4^3 Q_4^2$	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
		Ω^2	-106.04	Т2	-65.53	T2	-79.74
		Q2	100.01				
		Q2 Q2	-106.04	T2	-58.66	T2	-77.93

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