Supplementary Information.

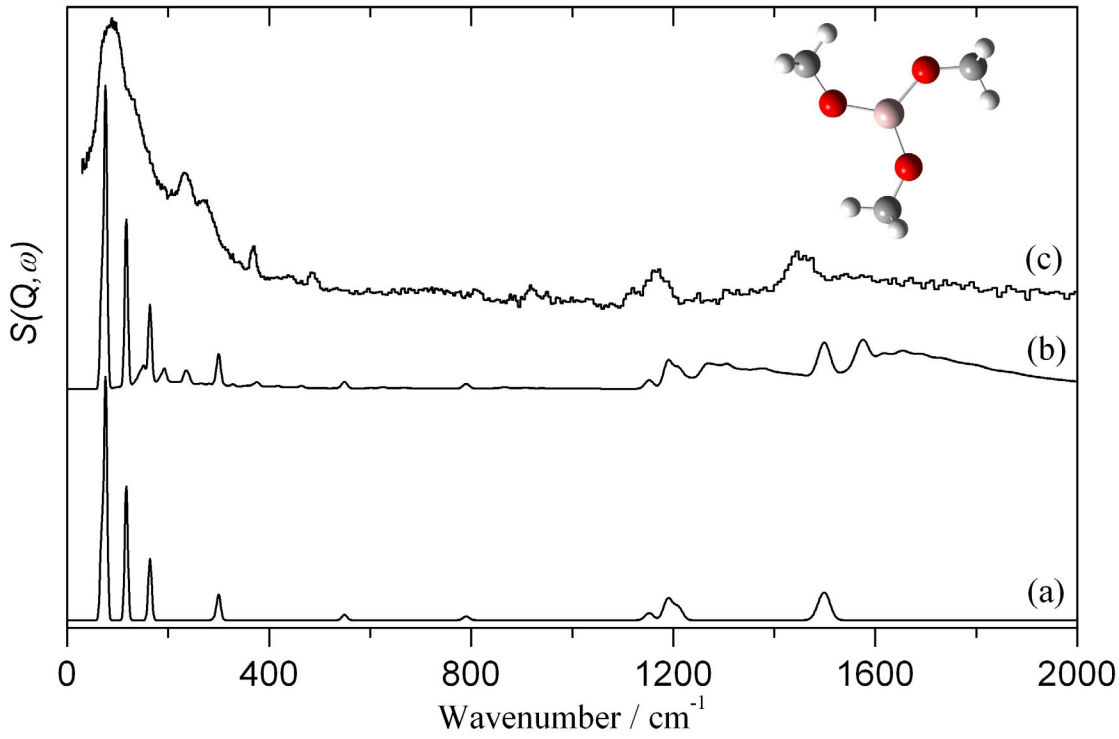

Figure S1. Comparison of the inelastic neutron scattering spectrum of $Al(OCH_3)_3$ with that calculated by DFT (B3LYP/6-31++g(2d,2p)). (a) Calculated spectrum, fundamentals only, (b) calculated spectrum including phonon wings, combinations and overtones (up to $n = 10$), (c) experimental spectrum. The planar C_{3h} structure used for the DFT calculation is shown at the top right.

Table S1. Comparison of calculated (B3LYP/6-31++g(2d,2p)) and observed INS frequencies for $Al(OCH_3)_3$.

Calc. / cm^{-1}	Expt. / cm^{-1}	Assignment
68		$AlO–CH_3$ oop bend A″
74	88 vs,br	CH_3 torsion E″
76		CH_3 torsion A″
77		$AlO–CH_3$ ip bend E′
117	232 s	Al–O oop bend E″
164	273 s	Al–O–C ip bend A′
293	368 m	Al–O oop bend A″
301		Al–O–C ip bend E′
550	487 w	Al–O sym stretch A′
[S2]791	808 w	Al–O asym stretch E′
1153	1117 m	$AlO–CH_3$ asym stretch E′
1154		$AlO–CH_3$ sym stretch A′
1190	1167 s	CH_3 rock E″
1190		CH_3 rock A″
1206		CH_3 rock E′
1211		CH_3 rock A′
1491		C–H sym bend A′
1491	1444 s	C–H sym bend E′
1500		C–H asym bend A″
1501		C–H asym bend E″
1504		C–H asym bend A′
1505	1468 s	C–H asym bend E′
3000		C–H sym stretch E′
3002		C–H sym stretch A′
3065		C–H asym stretch A′
3065		C–H asym stretch E′
3066		C–H asym stretch E″
3066		C–H asym stretch A″

s = strong, m = medium, w = weak, br = broad, v = very, oop = out-of-plane, ip = in-plane, sym = symmetric, asym = antisymmetric.

Note: The calculations were carried out assuming an isolated molecule of C_{3h} symmetry. The solid state structure of $Al(OCH_3)_3$ is not known although it is speculated (Amma E.L. *J. Inorg. Nucl. Chem.* **1963**, *25*, 779) that it is oligomeric or polymeric. If the speculation is correct, this would account for the differences observed in the low energy region.

Table S2. Comparison of experimental results for methoxy on η-alumina and calculated frequencies for methoxy on η-Al_2O_3(110).

Experimental / cm^{-1}		Calculated / cm^{-1}	Assignment
INS	Infrared		
		17, 88	Al–O–Al bend
		104	Al–O–CH_3 bend
140s		[S3]141	Al–O–CH_3 bend
96vs		151	CH_3 torsion
197s			(2 × CH_3 torsion)
280s			(2 × Al–O–CH_3 bend)
560w,br		198,220, 235, 244, 253, 261,266, 286, 312, 329, 336, 355, 380, 386, 400, 404, 410, 427, 448, 466, 475, 482, 538, 563, 569, 573, 591, 598, 611, 617, 655, 669, 678, 691, 706, 715, 787	Alumina lattice
936w		843	O–CH_3 stretch
1169m		1036, 1060	CH_3 rock
1265w			(CH_3 torsion + CH_3 rock)
	1452sh	1262	Symmetric CH_3 bend
1463m	1480s	1314, 1367	Antisymmetric CH_3 bend
2385vw			(2 × CH_3 rock)
2622w	2507,2607mw		(CH_3 rock + CH_3 bend)
	2820s	2840	Symmetric C–H stretch
2983s,br	2938s		Antisymmetric C–H
		2922, 2997	stretch

s = strong, m = medium, w = weak, br = broad, sh = shoulder, v = very

Full author list for reference 37.

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