Electronic Supplementary Information for:

"^{51}V NMR parameters of $VOCl_3$: Static and dynamic density functional study from the gas phase to the bulk."

Ragnar Bjornsson, Herbert Früchtl and Michael Bühl

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Table S1: Additional results for embedded cluster model I based on coordinates from X-ray crystallography (Troyanov 2005 and Galy et al 1983, see main paper); unoptimized: employing the raw experimental coordinates; other entries: optimized using the CPMD program and the functional indicated.[a]

		Gas	**Crystal**	**Crystal**	**Crystal**	**Crystal**	**Crystal**	**Crystal**
			Xray 2005	Xray 1983	Xray 2005	Xray 2005	Xray 1983	Xray 1983
		BP86-D	Unoptimized	Unoptimized	BP86-D	BP86	BP86-D	BP86
NMR-level:								
	σ_{iso}	-2267.6	-2179.3	-2133.2	-2269.1	-2246.7	-2259.4	-2243.2
B3LYP/	Gas-to-							
AE1	solid shift	-	-88.3	-134.5	+1.5	-20.9	-8.2	-24.5
	δ_σ	398.1	450.4	463.4	434.2	429.8	440.8	436.5
	η_σ	0.001	0.015	0.008	0.016	0.004	0.017	0.006
	C_Q	7.95	7.01	6.91	7.41	7.20	7.33	7.14
	η_Q	0.002	0.021	0.025	0.053	0.025	0.060	0.033
	σ_{iso}	-2334.2	-2245.2	-2197.9	-2337.4	-2314.6	-2327.5	-2311.1
B3LYP/	Gas-to-							
QZVPP	solid shift	-	-89.0	-136.3	+3.3	-19.6	-6.6	-23.1
	δ_σ	354.3	412.1	426.5	393.3	389.9	400.4	396.9
	η_σ	0.001	0.017	0.009	0.017	0.004	0.018	0.007
	C_Q	7.21	6.25	6.10	6.72	6.50	6.64	6.44
	η_Q	0.002	0.022	0.027	0.057	0.028	0.065	0.037

[a] Initial point charges used, cf. "run1" entries in Table S2.

Table S2: B3LYP solid-state NMR data of cluster model I (BP86-D geometry) with embedded point charges, showing the effect of point charge updates.

		B3LYP/AE1	B3LYP/QZVPP
Run 1. With point charges from a gas phase B3LYP/QZVPP calculation	σ_{iso}	-2269.1	-2337.4
	Gas-to-solid shift	-25.3	43.0
	δ_σ	434.21	393.3
	η_σ	0.016	0.017
	C_Q	7.41	6.72
	η_Q	0.053	0.057
Run 2: With point charges from embedded point charges from run 1.	σ_{iso}	-2269.4	-2337.9
	Gas-to-solid shift	-25.0	43.5
	δ_σ	441.5	400.8
	η_σ	0.017	0.020
	C_Q	7.38	6.69
	η_Q	0.051	0.055
Run 3: With point charges from embedded point charges from run 2.	σ_{iso}	-2269.4	-2338.0
	Gas-to-solid shift	-25.0	43.6
	δ_σ	442.4	401.7
	η_σ	0.017	0.0198
	C_Q	7.38	6.69
	η_Q	0.051	0.055

Table S3: Additional solid-state B3LYP NMR data with non-embedded and embedded[a] cluster models II but with different basis sets[b] for layer 2.

		Non-embedded	PC-embedded			Non-embedded	PC-embedded
σ_{iso}	Layer 1: AE1	-2287.2	-2286.8	Layer 1:	def2-QZVPP	-2349.9	-2349.5
Gas-to-solid shift	Layer 2: AE1	-19.5	-19.1	Layer 2:	AE1	-13.3	-13.8
δ_σ		441.7	447.1			403.4	409.1
η_σ		0.012	0.015			0.017	0.020
C_Q		7.31	7.28			6.86	6.84
η_Q		0.069	0.070			0.071	0.072
σ_{iso}	Layer 1: AE1	-2286.7	-2286.2	Layer 1:	def2-QZVPP	-2350.0	-2349.6
Gas-to-solid shift	Layer 2: 6-31G*	-19.1	-18.6	Layer 2:	6-31G*	55.6	55.2
δ_σ		442.6	447.2			405.2	410.4
η_σ		0.015	0.018			0.019	0.021
C_Q		7.33	7.31			6.80	6.78
η_Q		0.069	0.070			0.072	0.073
σ_{iso}	Layer 1: AE1	-2287.1	-2286.7	Layer 1:	def2-QZVPP	-2350.3	-2349.9
Gas-to-solid shift	Layer 2: 6-31G	-19.5	-19.1	Layer 2:	6-31G	55.9	55.5
δ_σ		456.4	460.8			418.9	423.9
η_σ		0.029	0.031			0.034	0.036
C_Q		7.32	7.30			6.81	6.80
η_Q		0.067	0.068			0.072	0.073
σ_{iso}	Layer 1: AE1	-2290.5	-2288.9	Layer 1:	def2-QZVPP	-2346.4	-2345.5
Gas-to-solid shift	Layer 2: STO-3G	-22.9	-21.3	Layer 2:	STO-3G	52.0	51.1
δ_σ		426.8	429.0			387.5	390.8
η_σ		0.068	0.072			0.063	0.066
C_Q		7.57	7.56			6.87	6.86
η_Q		0.070	0.070			0.080	0.081

[a]Point charges not updates (cf. run1 in Table S2).

[b]6-31G and 6-31G* basis on vanadium from: V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.* **1998**, *109*, 1223.

Table S4. Additional chemical shift and quadrupole coupling data with a single molecule (gas-phase optimized)and two different cluster models of the solid state (with and without embedded point charges), cf. Table 2 in main paper.[a]

	Single molecule	**Cluster I**		**Cluster II**	
B3LYP/QZ/ 6-31G*	Gas phase optimized	Non-embedded	PC-embedded	Non-embedded	PC-embedded
σ_{iso}	-2351.6	-2352.6	-2354.3	-2365.4	-2364.7
Gas-to-solid shift	0.0	-1.1	-2.8	-13.8	-13.1
δ_σ	359.3	341.5	408.2	407.1	413.6
η_σ	0.001	0.014	0.018	0.014	0.017
C_Q	7.00	6.66	6.49	6.62	6.60
η_Q	0.002	0.063	0.052	0.068	0.069

[a]B3LYP/QZVPP/6-31G* as the level in layer 1.

Table S5: Input parameters for "on-the-fly generation" of pseudopotentials in CASTEP. Set 1 was used to generate the data discussed in the text, set 2 is the one mentioned in reference 40.

Set	Default setting in	OTF String

1	CASTPEP 5.0	`O 2|1.0|1.3|0.7|13|16|18|20:21(qc=7)`
		`Cl 2|1.7|1.7|1.2|6|7|8|30:31:32LGG`
		`V 3|2.0|2.0|1.4|10|12|13|30U:40U:31:32(qc=6)`

2	Materials Studio[a]	`O 2|1.3|16.537|18.375|20.212|20UU:21UU(qc=7.5)[]`
		`Cl 2|1.7|5.88|7.35|9.187|30UU:31UU:32LGG[]`
		`V 3|2|2|1.4|10|13|15|30U=-3.06:40U=-0.465:31U=-2.105U=+0.1:32U=-1.15U=+0.1[]`

[a]See http://ccpforge.cse.rl.ac.uk/frs/download.php/293/otfg.cell (accessed 13 July 2010).

Table S6: Dependence of η_Q at the ^{51}V nucleus on the displacement of a single Cl atom from the CP-opt equilibrium geometry of gaseous $VOCl_3$ (GIAO-B3LYP/AE1 level).

Parameter	Deviation[a]	η_Q
r(V-Cl)	+0.1 Å	0.25
"	–0.1 Å	0.31
a(O=V-Cl)	+6º	0.05
"	–6º	0.01
θ(OVClCl)[b]	+6º	0.45

[a]From the CP-opt equilibrium value (roughly corresponding to twice the standard deviation encountered in the CPMD simulations in the gas phase).
[b]O-V-Cl-Cl dihedral angle, describing the bending of one Cl atom out of the mirror plane of the C_{3v} minimum.