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Supporting Information

for

DFT Study of the NMR Properties of Xenon in Covalent Compounds and van der Waals Complexes. Implications for the Use of ^{129}Xe as Molecular Probe

By

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Tables S1-S14: Calculated nuclear shieldings, chemical shifts and coupling constants of ^{129}Xe in covalent compounds and van der Waals complexes

All DFT calculations run with BP functional, except for Table S1

Table S1. Spin-spin coupling constants J_{XeO} and J_{XeF} in $XeOF_4$ with various functionals available in ADF. Non-relativistic level Xe.4p and all-electron for O and F. Experimental values are 692 Hz and 1115/1131 Hz, respectively.[a]

	J_{XeO}				J_{XeF}			
	PSO	**FC**	**SD**	**TOT**	**PSO**	**FC**	**SD**	**TOT**
BP[56,58]	-203	-467	14	-656	292	-1151	-138	-997
PW91[52]	-204	-469	15	-658	297	-1145	-136	-985
PBE[53]	-201	-466	15	-653	294	-1133	-135	-974
RPBE[54]	-198	-461	14	-645	294	-1096	-134	-937
revPBE[55]	-198	-462	14	-647	292	-1101	-135	-945
BLYP[56,57]	-215	-476	15	-676	310	-1152	-141	-983

[a]References to the functionals used are given in brackets (see the paper).

Table S2. Spin-spin coupling constants J_{XeF} in XeF_2 and XeF_4 at the relativistic (scalar and spin-orbit) levels with various basis sets available in ADF. Experimental values are 5550/5665 Hz and 3801/3900 Hz respectively.

		XeF_2				XeF_4			
		PSO	**FC**	**SD**	**TOT**	**PSO**	**FC**	**SD**	**TOT**
Scalar	DZ	-3111	-2252	-992	-6355	-433	-2863	-389	-3686
	TZP	-3057	-2163	-991	-6211	-356	-2823	-395	-3575
	TZ2P	-2979	-1998	-981	-5958	-258	-2587	-375	-3221
	QZ4P	-3039	-2133	-1004	-6176	-246	-2785	-381	-3413
Spin-Orbit	DZ	-3092	-3141		-6233	-598	-3461		-4060
	TZP	-3024	-3104		-6129	-526	-3505		-4031
	TZ2P	-2932	-2916		-5949	-431	-3248		-3679
	QZ4P	-3046	-3185		-6231	-445	-3523		-3968

Covalent compounds

Table S3. Calculated shielding constants and chemical shifts (ppm) with DFT and *ab initio* non-relativistic methods.

	DFT[a]				MP2[b]				
	p	d			p	d			exp
Xe	0	5642	5642	–4689	0	5638	5638	–4027	–5331
XeF_2	–2876	5631	2755	–1802	–2751	5632	2880	–1269	–1592; –2009
$FXeO(SO_2F)$	–3221	5631	2410	–1457					–1407; –1666
$FXeN(SO_2F)_2$	–2959	5631	2672	–1719					–1997; –2053
XeF_4	–4955	5621	666	287	–4361	5626	1265	–346	166.1; 259
XeO_2F_2	–4649	5627	977	–24					17; 73
$XeOF_4$	–4670	5623	953	0	–4013	5625	1611	0	0
XeO_3	–4823	5631	808	145					217
XeF_6	–4868	5619	751	202					–35; –45
XeF^+	–6435	5633	–802	1755					–574; –911
$XeCl^+$	–1798	5636	3838	–2885					–551

[a]BP/TZP, *Xe*.4*p* frozen core basis. [b]MP2/DZVP.

Table S4. Calculated coupling constants (Hz): non-relativistic, TZP, *Xe*.4*p* frozen core basis.

		PSO	FC	SD	TOT	J_{exptl}
XeF_2	$^1J_{XeF}$	–2737	–1675	–920	–5332	5550; 5665
$FXeO(SO_2F)$	$^1J_{XeF}$	–3228	–1368	–1036	–5632	5830; 6051
$FXeN(SO_2F)_2$	$^1J_{XeF}$	–3049	–1522	–1013	–5584	5572; 5624
	$^1J_{XeN}$	46.3	118.9	18.5	183.7	307.4
	$^3J_{XeF}$	6.5	–16.9	–4.7	–15.1	18
XeF_4	$^1J_{XeF}$	–321	–2306	–369	–2996	3801; 3900
XeO_2F_2	$^1J_{xeF}$	61.1	–687	–141	–767	1217
	$^1J_{XeO}$	–168	–362	8.6	–521	521
$XeOF_4$	$^1J_{XeF}$	292	–1151	–138	–997	1115; 1131
	$^1J_{XeO}$	–203	–467	14.0	–656	692
XeF_6 [a]	$^1J_{XeF}$	636	–2161	–153	–1678	330
XeF^+	$^1J_{XeF}$	–8590	–245	–3160	–11995	6703; 7594
$XeCl^+$	$^1J_{XeCl}$	–1277	–67.7	–456	–1801	5165

[a]Average of the results obtained for the two non equivalent fluorine atoms in C_{3v} structure.

Table S5. Calculated shielding constants and chemical shifts (ppm): spin-orbit relativistic ZORA/TZ2P level.

	p	**d**	**SO**			**exp**
Xe	80	5582	747	6409	–5656	–5331
XeF_2	–3454	5574	894	3014	–2261	–1592; –2009
$FXeO(SO_2F)$	–3722	5575	910	2763	–2010	–1407; –1666
$FXeN(SO_2F)_2$	–3403	5575	879	3051	–2298	–1997; –2053
XeF_4	–5788	5568	592	372	381	166.1; 259
XeO_2F_2	–5278	5574	622	919	–166	17; 73
$XeOF_4$	–5361	5569	545	753	0	0
XeO_3	–5423	5578	676	831	–78	217
XeF_6	–5442	5564	472	594	159	–35; –45
XeF^+	–7123	5573	1596	48	705	–574; –911
$XeCl^+$	–2354	5578	1081	4304	–3551	–551

Table S6. Calculated coupling constants (Hz): spin-orbit relativistic ZORA/TZ2P level.

		PSO	**FC + SD**	**TOT**	$J_{\mathbf{exptl}}$
XeF_2	$^1J_{XeF}$	–2932	–2916	–5848	5550; 5665
$FXeO(SO_2F)$	$^1J_{XeF}$	–3396	–2712	–6108	5830; 6051
$FXeN(SO_2F)_2$	$^1J_{XeF}$	–3150	–2792	–5942	5572; 5624
	$^1J_{XeN}$	49	210	259	307.4
	$^3J_{XeF}$	5.8	–24.5	–18.7	18
XeF_4	$^1J_{XeF}$	–431	–3248	–3679	3801; 3900
XeO_2F_2	$^1J_{xeF}$	108	–1393	–1286	1217
	$^1J_{XeO}$	–186	–300	–486	521
$XeOF_4$	$^1J_{XeF}$	370	–1955	–1585	1115; 1131
	$^1J_{XeO}$	–220	–397	–617	692
XeF_6 [a]	J_{XeF}	669	–3036	–2367	330
XeF^+	$^1J_{XeF}$	–8034	–2268	–10302	6703; 7594
$XeCl^+$	$^1J_{xeCl}$	–1164	–355	–1519	5165

[a] Average of the results obtained for the two non equivalent fluorine atoms in C_{3v} structure.

Van der Waals Complexes

Table S7. Xe···Xe dimer, shielding parameters (ppm).

R **(Å)**			$\perp$	$\parallel$
4.0	81.9353	126.761	5536.311	5663.072
4.2	52.881	82.665	5580.064	5662.729
4.4	33.847	53.775	5608.728	5662.503
4.6	21.6977	35.164	5627.081	5662.245
4.8	14.0047	23.248	5638.746	5661.994
5.0	9.24	15.969	5645.937	5661.906
5.2	6.26067	11.302	5650.472	5661.774
5.6	3.12833	6.284	5655.277	5661.561
6.0	1.702	3.783	5657.537	5661.320
6.5	0.782333	2.144	5659.003	5661.147

Table S8. Xe···Xe dimer, through-space coupling parameters (Hz).

R **(Å)**	**DSO**	**PSO**	**FC**	**SD**	**TOT**
4.0	0.000	–38.490	66.454	3.407	31.371
4.2	0.000	–25.699	32.775	2.774	9.850
4.4	0.000	–16.708	15.838	2.087	1.217
4.6	0.000	–10.616	7.509	1.479	–1.627
4.8	0.000	–6.556	3.488	0.997	–2.071
5.0	0.000	–4.027	1.588	0.644	–1.796
5.2	0.000	–2.432	0.706	0.401	–1.326
5.6	0.000	–0.860	0.127	0.139	–0.594
6.0	0.000	–0.301	0.018	0.041	–0.242
6.5	0.000	–0.078	0.000	0.006	–0.072

Table S9. Xe···CH_4 dimer **1**, shielding parameters (ppm).

R **(Å)**			x	y	z
3.5	120.629	166.429	5469.727	5499.063	5650.824
3.8	63.338	87.846	5561.742	5574.018	5655.726
4.0	40.549	56.07	5598.162	5604.360	5657.331
4.2	25.671	35.31	5621.882	5624.236	5658.369
4.4	16.259	22.0935	5636.900	5636.853	5658.970
4.6	10.4457	13.939	5646.181	5644.635	5659.347
5.0	4.89167	6.3055	5654.938	5652.075	5659.812
5.4	2.974	3.855	5657.727	5654.755	5660.096
6.0	1.948	2.6325	5658.697	5656.652	5660.307

Table S10. Xe···CH_4 dimer **1**, through-space coupling parameters (Hz).

	J_{XeC}					J_{XeH1}[a]					J_{XeH2}[b]				
R **(Å)**	**DSO**	**PSO**	**FC**	**SD**	**TOT**	**DSO**	**PSO**	**FC**	**SD**	**TOT**	**DSO**	**PSO**	**FC**	**SD**	**TOT**
3.5	–0.00	3.17	–21.47	–0.16	–18.47	–0.16	0.51	–9.79	0.48	–8.96	0.17	0.32	–5.16	0.07	–4.62
3.8	0.00	1.70	–7.80	–0.13	–6.24	–0.14	0.27	–4.83	0.26	–4.44	0.14	0.11	–2.76	0.03	–2.48
4.0	0.00	1.08	–3.85	–0.10	–2.87	–0.13	0.19	–2.82	0.17	–2.59	0.13	0.03	–1.74	0.02	–1.56
4.2	0.00	0.67	–1.85	–0.08	–1.25	–0.12	0.15	–1.57	0.10	–1.44	0.12	–0.02	–1.06	0.01	–0.95
4.4	0.00	0.41	–0.87	–0.05	–0.51	–0.11	0.12	–0.85	0.06	–0.77	0.11	–0.04	–0.62	0.01	–0.55
4.6	0.00	0.24	–0.39	–0.04	–0.18	–0.10	0.11	–0.45	0.04	–0.40	0.10	–0.06	–0.36	0.00	–0.31
5.0	0.00	0.08	–0.08	–0.01	–0.01	–0.08	0.09	–0.15	0.01	–0.13	0.08	–0.06	–0.11	0.00	–0.09
5.4	0.00	0.03	–0.01	–0.00	0.01	–0.07	0.07	–0.07	0.00	–0.07	0.07	–0.06	–0.03	0.00	–0.02
6.0	0.00	0.01	0.00	–0.00	0.01	–0.06	0.06	–0.04	0.00	–0.04	0.06	–0.05	–0.01	0.00	0.00

[a]Coupling with the closest hydrogens (see Figure 2). [b]Coupling with the farthest hydrogens (see Figure 2).

Table S11. Xe···benzene dimer **2**, shielding parameters (ppm).

***R* (Å)**			⊥	∥
3.2	32.3017	35.284	5616.445	5651.717
3.4	12.5463	12.148	5643.911	5656.059
3.6	2.327	1.021	5657.821	5658.842
3.8	–2.294	–3.434	5663.926	5660.492
4.0	–3.86433	–4.475	5665.855	5661.380
4.2	–3.90667	–3.842	5665.687	5661.845
4.4	–3.33133	–2.782	5664.759	5661.977
4.8	–1.86467	–0.731	5662.608	5661.877
5.2	-0.803333	0.625	5661.097	5661.719
5.6	-0.213333	1.267	5660.293	5661.557
6.0	0.009	1.495	5659.994	5661.487
6.5	0.044666	1.422	5659.982	5661.403

Table S12. Xe···benzene dimer **2**, through-space coupling parameters (Hz).

			J_{XeC} **(Hz)**					J_{XeH} **(Hz)**		
***R* (Å)**	**DSO**	**PSO**	**FC**	**SD**	**TOT**	**DSO**	**PSO**	**FC**	**SD**	**TOT**
3.4	–0.03	0.36	–2.36	0.00	–2.02	0.08	–0.05	0.36	–0.04	0.35
3.6	–0.02	0.23	–1.22	–0.00	–1.01	0.07	–0.04	0.23	–0.03	0.23
3.8	–0.02	0.14	–0.61	–0.00	–0.49	0.06	–0.04	0.14	–0.01	0.15
4.0	–0.02	0.09	–0.30	0.00	–0.23	0.05	–0.03	0.09	–0.01	0.10
4.2	–0.01	0.06	–0.15	–0.00	–0.11	0.05	–0.03	0.06	–0.00	0.07
4.4	–0.01	0.04	–0.07	–0.00	–0.05	0.04	–0.02	0.03	–0.00	0.05
4.8	–0.01	0.02	–0.02	–0.00	–0.02	0.03	–0.01	0.01	–0.00	0.03

Table S13. Benzene ···Xe···benzene complex **3**, shielding parameters (ppm).

***R* (Å)**			⊥	∥
3.2	74.2017	80.932	5559.321	5640.253
3.4	32.6937	33.229	5616.730	5649.959
3.6	10.7777	9.43	5646.579	5656.009
3.7	4.49067	3.016	5655.004	5658.020
3.8	0.291667	–1.013	5660.546	5659.533
3.9	–2.38367	–3.331	5663.994	5660.663
4.0	–3.93933	–4.403	5665.907	5661.504
4.1	–4.72933	–4.754	5666.814	5662.060
4.2	–4.97867	–4.555	5666.997	5662.442
4.4	–4.59867	–3.388	5666.228	5662.840
4.6	–3.64833	–1.925	5664.790	5662.865
5.0	–1.743	0.705	5662.008	5662.713

Table S14. Xe···O[Si(OH)$_3$]$_2$ dimer **4**, shielding parameters (ppm).

R **(Å)**			**x**	**y**	**z**
3.0	141.85	161.448	5437.887	5491.782	5626.282
3.4	68.7013	80.384	5553.035	5576.973	5645.388
3.8	31.806	37.7325	5610.236	5621.997	5653.849
4.2	15.444	18.663	5636.410	5641.260	5657.498
4.6	8.89233	11.1875	5647.582	5648.175	5659.066
5.0	6.368	8.127	5650.273	5652.573	5659.550
5.4	5.113	6.486	5651.576	5654.874	5659.711
5.8	4.11267	5.3305	5652.920	5656.301	5659.941
6.5	2.437	3.5655	5655.768	5657.981	5660.440