Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information:

Theoretical predictions of the spectroscopic parameters in noble-gas molecules: HXeOH and its complex with water

Janusz Cukras and Joanna Sadlej

Comments to Table II Some methodological aspects of the calculations should be discussed: the comparison of the non-relativistic results (P3) versus ECP-relativistic results (aug-cc-pVTZ(-PP)) (Table II). The total SAPT energies for the latter are in agreement with the corresponding supermolecular interaction energies for P3 basis set. The slightly smaller values of E_{elst} and E_{exch} in comparison with P3 basis set may be attributed to a smaller basis set. There are, however, some differences in E_{ind} and E_{disp} that need a comment. The dispersion term doubles for the α complex as compared to P3 results, similarly for δ and γ structures, but to a lesser extent. Induction term essentially remains unchanged for α, whereas it decreases ca. two and three times for δ and γ structures, respectively. The overall relative contributions to total SAPT interaction energy are also changed. For instance, the relative contributions of E_{ind} and E_{disp} in the α structure are 51% and 54% for aug-cc-pVTZ(-PP) basis set and make this structure induction-dispersion stabilized. The δ structure is characterized by the induction/dispersion ratio of 66%:41% in P3 basis, while it becomes 35%:73% in aug-cc-pVTZ(-PP) basis set. These changes, however, cannot be attributed to any kind of relativistic effect because of the difference in the number of basis set functions applied in each calculation. Moreover, the ECP approximation, as applied and tested in SAPT software suite, may lead to inaccurate results in induction and exchange-induction terms and, thus, poorly reproduce the SCF level contribution [**?**]. The total SAPT energy, however, is well reproduced when the $\delta E^{HF}_{int,resp}$ is used. Indeed, this is the case, since the total SAPT values agree well with the corresponding P3 results. This is why we focus on P3 results when analyzing individual contributions. Applying Douglas-Kroll approximation to SAPT calculations does not qualitatively affect the results. The largest change in total SAPT interaction energy occurs for SAPT0 energy and it is not larger in absolute value than 3% of the non-relativistic result.

Table I: A comparison of frequencies [cm^{-1}] and IR intensities [km/mol] calculated with P3 basis set obtained for H_2O, $(H_2O)_2$, HXeOH and α-HXeOH$\cdots H_2O$

	H_2O			HXeOH			$(H_2O)_2$			α-HXeOH$\cdots H_2O$		
	Vibration	ν	I	Vibration	ν	I	Vibration	ν	I	Vibration	ν	I
Intramolecular				ν_{O3Xe7}	425	119.9				ν_{XeO3}	398	150.7
				$\nu_{H1O3Xe7} + \nu_{O3Xe7H2}$	568	3.0						
				$\nu_{O3Xe7H2}$	628	0.1				$\nu^{\text{out of plane}}_{O3Xe7H2}$	616	12.4
				$\nu_{H1O3Xe7} - \nu_{O3X37H2}$	779	60.1						
	ν_{H1O2H3}	1617	104.7				ν_{H4O5H6}	1628	112.5	ν_{H4O5H6}	1657	138.7
							ν_{H1O2H3}	1675	110.1			
				ν_{Xe7H2}	1748	1292.5				ν_{Xe7H2}	1895	830.6
	$\nu_{O3H1} + \nu_{O3H2}$	3598	1.5	ν_{O3H1}	3554	28.0	$\nu_{O5H4} + \nu_{O5H6}$	3494	296.3	ν_{O5H4}	3207	743.4
	$\nu_{O3H1} - \nu_{O3H2}$	3788	36.8				$\nu_{O3H1} + \nu_{O3H2}$	3632	0.2	ν_{O3H1}	3617	24.0
							$\nu_{O5H4} - \nu_{O5H6}$	3754	107.7	ν_{O5H6}	3740	45.8
							$\nu_{O3H1} - \nu_{O3H2}$	3807	73.5			
Intermolecular												
								138	102.3		59	28.3
								213	35.2		156	91.0
								239	121.8		191	292.0
								243	315.2		292	24.0
								415	250.8		533	138.9
								840	272.4		592	62.6
											773	92.5
											871	170.4

Table II: SAPT calculations of the interaction energy of the α, δ, γ-HXeOH$\cdots$$H_2O$ complexes [kJ/mol] with different basis sets. $(H_2O)_2$ data for comparison.

	aug-cc-pVTZ(-PP)				P3				P3+mbf[c)]				DK-P3			
SAPT term	α	δ	γ	$(H_2O)_2$	α	δ	γ	$(H_2O)_2$	α	δ	γ	$(H_2O)_2$	α	δ	γ	$(H_2O)_2$
E^{HF}_{int}	-33.40	-6.99	-5.90	-15.09	-54.87	-9.72	-17.4	-26.67	-41.87	-2.43	-8.87	-20.98	-56.45	-9.08	-17.26	-26.57
$E^{(10)}_{elst}$	-82.29	-26.20	-18.39	-35.17	-104.12	-35.69	-44.82	-55.38	-89.88	-28.43	-38.85	-48.77	-105.00	-35.20	-44.66	-55.26
$E^{(10)}_{exch}$	77.26	25.75	19.32	29.73	83.72	37.58	46.87	43.83	82.75	36.58	47.87	42.94	83.24	37.69	47.13	43.80
$E^{(20)}_{ind,resp}$	-42.13	-9.94	-9.17	-12.74	-46.04	-15.65	-24.89	-19.15	-45.52	-14.58	-23.78	-19.02	-46.03	-15.66	-25.10	-19.14
$E^{(20)}_{ex-ind,r}$	23.84	6.29	5.78	7.01	24.94	9.24	15.51	10.40	24.57	9.04	16.06	10.33	24.77	9.29	15.60	10.40
$E^{(30)\,\mathrm{b)}}_{ind}$	-59,58	-12.45	-15.21	-11.86	-61.43	-20.13	-45.03	-19.28				-18.94	-60.61	-20.26	-45.20	-19.29
$E^{(30)}_{ex-ind}$	48.86	11.43	14.25	10.72	56.55	18.85	43.19	17.44				17.03	55.71	18.99	43.29	17.45
$SAPTSCF_{resp}$	-23.33	-4.09	-2.45	-11.18	-41.50	-4.51	-7.33	-20.30	-28.06	2.6	1.30	-14.53	-43.03	-3.87	-7.02	18.45
$\delta^{HF}_{int,r}$	-10.08	-2.90	-3.45	-3.91	-13.37	-5.21	-10.08	6.37	-13.80	-5.03	-10.17	-6.46	-13.42	-5.21	-10.24	-6.37
$E^{(12)}_{elst,resp}$	3.69	-1.62	1.61	0.38	6.09	-4.76	0.67	-0.07	5.94	-2.84	1.51	0.24	6.79	-5.09	0.85	-0.06
$E^{(13)}_{elst,resp}$	0.00	1.59	0.24	0.63	-1.43	3.3	0.92	1.23	-1.67	2.33	0.83	0.72	-1.69	3.47	0.88	1.23
$E^{(11)}_{exch}$	0.95	0.16	0.52	0.39	-1.61	-1.24	-0.21	-0.79	0.39	-0.2	1.11	-0.17	-1.59	-1.25	-0.17	-0.79
$E^{(12)}_{exch}$	12.88	5.80	2.71	4.18	17.19	10.22	8.65	8.41	16.38	9.64	8.23	8.43	17.22	10.34	8.91	8.41
$\epsilon^{(1)}_{exch}(CCSD)$	13.01	5.42	3.27	4.79	16.45	9.26	11.29	9.24	16.55	9.22	11.74	9.71	16.29	9.27	11.61	9.24
${}^{t}E^{(22)}_{ind}$	-7.84	-2.67	-1.41	-1.86	-8.88	-4.53	-5.09	-3.40	-8.65	-4.39	-4.84	-3.42	-8.83	-4.61	-5.24	-3.40
${}^{t}E^{(22)}_{ex-ind}*$	4.44	1.69	0.89	1.02	4.81	2.67	3.17	1.84	4.67	2.72	3.27	1.86	4.75	2.74	3.26	1.85
$E^{(20)}_{disp}$	-28.66	-11.90	-10.24	-10.77	-14.02	-6.66	-8.45	-6.16	-26.93	-13.93	-17.79	-10.9	-13.97	-6.68	-8.56	-6.17
$E^{(21)}_{disp}$	3.21	0.45	1.07	0.2	1.48	-0.08	0.92	-0.09	2.33	0.17	1.50	-0.15	1.50	-0.07	0.97	-0.09
$E^{(22)}_{disp}$	-6.86	-2.87	-2.39	-1.96	-4.66	-1.95	-2.37	-1.43	-7.48	-3.88	-4.60	-2.48	-4.71	-1.97	-2.44	-1.43
$E^{(20)}_{exch-disp}$	5.72	2.17	1.84	1.97	3.32	1.56	2.03	1.34	5.51	2.76	3.76	2.18	3.30	1.57	2.05	1.34
$E^{(30)}_{ind-disp}$	-8.37	-2.67	-2.19	-2.71	-5.74	-2.57	-4.13	-2.48				-2.89	-5.70	-2.59	-4.19	-2.48
$E^{(30)}_{ex-ind-disp}$	7.61	2.39	2.24	2.27	5.51	2.32	3.75	2.15				2.52	5.48	2.34	3.79	2.15
$E^{(30)}_{disp}$	0.87	0.40	0.33	0.4	-0.16	-0.07	-0.1	-0.05				0.21	-0.16	-0.07	-0.10	-0.05
$E^{(30)}_{exch-disp}$	-0.43	-0.19	-0.18	-0.17	0.13	0.05	0.04	0.04				-0.1	0.13	0.05	0.04	0.04
$SAPT_{corr,resp}$	-13.29	-7.73	-5.12	-5.6	3.16	-1.18	3.09	2.51	-9.73	-7.83	-4.62	-2.25	3.43	-1.38	3.38	2.51
E_{elst}	-78.61	-27.82	-16.77	-34.78	-98.03	-40.45	-44.15	-55.45	-83.94	-31.27	-37.34	-48.53	-98.22	-40.29	-43.81	-55.33
E_{exch}	91.09	31.71	22.55	34.29	99.3	46.57	55.31	51.45	99.53	46.01	57.21	51.2	98.87	46.79	55.87	51.42
E_{ind}	-21.7	-4.63	-3.91	-6.57	-25.17	-8.26	-11.3	-10.31	-24.92	-7.21	-9.29	-10.26	-25.34	-8.24	-11.48	-10.29
E_{disp}	-22.93	-9.73	-8.4	-8.8	-10.7	-5.1	-6.42	-4.82	-21.42	-11.16	-14.03	-8.73	-10.67	-5.11	-6.50	-4.83
[a)] $SAPT0$	-46.26	-13.82	-10.85	-19.98	-52.2	-9.61	-13.75	-25.11	-49.48	-8.56	-12.72	-23.25	-53.69	-8.99	-13.52	-25.03
$SAPT2$	-42.22	-13.36	-9.98	-19.78	-47.97	-12.46	-16.64	-25.49	-44.55	-8.67	-13.61	-22.77	-48.78	-12.06	-16.15	-25.40
$SAPT$	-46.69	-14.73	-11.02	-20.69	-51.71	-10.9	-14.31	-24.15	-51.60	-10.26	-13.48	-23.23	-53.02	-10.46	-13.88	-24.07
$SAPT3$	-47.65	-12.92	-8.33	-18.14	-43.48	-7.23	-6.52	-19.96				-18.95	-44.74	-6.79	-6.00	-19.87

[a)] The notation - see the text.

[b)] The new implementation of the SAPT2008 code contains some third-order terms. We introduce them denoting this level of SAPT calculations as E^{SAPT3}_{int}:

$$E^{SAPT3}_{int} = E^{SAPT}_{int} + E^{(30)}_{ind} + E^{(30)}_{ind-disp} + E^{(30)}_{disp} + E^{(30)}_{exch-ind} + E^{(30)}_{exch-ind-disp} + E^{(30)}_{exch-disp} - \delta E^{HF}_{int,resp}. \qquad (1)$$

It is important to note that this level does not include $\delta E^{HF}_{int,resp}$ because the terms $E^{(30)}_{ind}$ and $E^{(30)}_{exch-ind}$ are part of it [**? ? ?**].

[c)] Due to high cost, third-order terms of SAPT were not calculated for complexes with midbond functions.

Table III: NMR shielding constants [ppm] for the ^{1}H, ^{17}O and ^{129}Xe nuclei in H_2O, HXeOH and α, δ, γ-HXeOH···H_2O complexes (at MP2/aug-cc-pVTZ(-PP) geometry) by different methods

SCF/aug-cc-PVTZ(-PP)

at.	Xe	H_2O	HXeOH	Δw	$(H_2O)_2$	α	Δc	δ	Δc	γ	Δc
H1		31	31	1	30	31	1	30	0	30	0
H2		31	27	-4	30	27	-3	30	0	30	0
O3 (in O3···H4)		327	147	-180	320	168	-152	318	-2	320	0
H4 (in O3···H4)					27	24	-4	28	1	26	-2
O5					326	318	-8	137	-189	152	-174
H6					31	31	0	27	-4	32	1
Xe7	515		458			461		457		457	

MP2/aug-cc-PVTZ(-PP)

at.	Xe	H_2O	HXeOH	Δw	$(H_2O)_2$	α	Δc	δ	Δc	γ	Δc
H1		31	29	-2	30	29	-1	30	0	30	0
H2		31	25	-5	30	26	-4	30	0	30	0
O3 (in O3···H4)		345	155	-189	337	171	-166	336	-1	338	1
H4 (in O3···H4)					28	24	-3	26	-1	24	-3
O5					340	330	-10	138	-202	164	-176
H6					31	31	0	25	-6	29	-2
Xe7	515		459			461		458		456	

$^{a)}\Delta w = \sigma(X, HXeOH) - \sigma(X, H_2O)$, $\Delta c = \sigma(X, complex) - \sigma(X, (H_2O)_2)$

Table IV: NMR spin-spin coupling constants [Hz] for the ^{1}H and ^{17}O nuclei in $(H_2O)_2$ at MP2/aug-cc-pVTZ(-PP) geometry

	constant	SCF/P3					DHF/P3	B3LYP/P3					CCSD/P3				
		J^{tot}	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}	J^{tot}	J^{tot}	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}	J^{tot}	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}
$(H_2O)_2$																	
Intramolecular	$^1J_{\text{O3-H1}}$	-99.3	-88.9	0.4	-10.5	-0.2	-99.0	-66.9	-56.5	-0.1	-10.0	-0.2	-80.2	-70.6	-0.1	-9.3	-0.2
	$^1J_{\text{O3-H2}}$	-99.3	-88.9	0.4	-10.5	-0.2	-99.0	-66.8	-56.4	-0.1	-10.0	-0.2	-80.3	-70.6	-0.1	-9.3	-0.2
	$^1J_{\text{O5-H4}}$	-101.3	-92.9	0.4	-8.4	-0.3	-100.9	-66.4	-58.1	0.0	-8.0	-0.3	-80.6	-73.0	0.1	-7.4	-0.3
	$^1J_{\text{O5-H6}}$	-93.5	-81.6	0.4	-12.0	-0.3	-93.2	-61.9	-49.9	-0.2	-11.5	-0.3	-76.8	-65.9	-0.1	-10.6	-0.3
	$^2J_{\text{H1-H2}}$	-26.1	-25.7	1.6	4.3	-6.3	-26.1	-10.4	-9.9	1.2	4.5	-6.3	-14.0	-13.3	1.2	4.3	-6.2
	$^2J_{H6-H4}$	-25.3	-24.9	1.6	3.9	-5.9	-25.4	-10.0	-9.5	1.2	4.1	-5.8	-13.7	-13.0	1.2	3.8	-5.8
Intermolecular	$^{1h}J_{\text{O3-H4}}$	9.3	9.7	-0.4	0.4	-0.4	9.3	5.9	6.4	-0.4	0.3	-0.4	5.3	5.7	-0.3	0.4	-0.4
	$^{2h}J_{\text{H4-H1}}$	0.7	0.5	0.1	0.2	-0.1	0.6	0.2	0.0	0.1	0.2	-0.1	0.4	0.2	0.1	0.1	-0.1
	$^{2h}J_{\text{H4-H2}}$	0.7	0.5	0.1	0.1	-0.1	0.7	0.2	0.0	0.1	0.1	-0.1	0.3	0.2	0.1	0.2	-0.1
	$^{2h}J_{\text{O5-O3}}$	2.4	2.6	0.1	-0.4	0.0	2.4	-0.3	0.0	0.1	-0.4	0.0	1.2	1.4	0.1	-0.3	0.0
	$^{3h}J_{\text{O3-H6}}$	1.0	0.9	0.0	0.0	0.1	1.0	0.5	0.4	0.0	0.0	0.1	0.6	0.5	0.0	0.0	0.1
	$^{3h}J_{\text{O5-H2}}$	0.4	0.4	0.0	0.0	0.1	0.4	0.3	0.3	0.0	0.0	0.1	0.3	0.2	0.0	0.0	0.1
	$^{3h}J_{\text{O5-H1}}$	0.4	0.4	0.0	0.0	0.1	0.4	0.3	0.3	0.0	0.0	0.1	0.3	0.2	0.0	0.0	0.1
	$^{4h}J_{\text{H6-H1}}$	-0.9	0.0	0.0	0.8	-1.7	-0.9	-0.9	-0.1	0.0	0.8	-1.7	-0.9	0.0	0.0	0.8	-1.7
	$^{4h}J_{\text{H6-H2}}$	-0.9	0.0	0.0	0.8	-1.7	-0.9	-0.9	-0.1	0.0	0.8	-1.7	-0.9	0.0	0.0	0.8	-1.7