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Hydrogen bonding to xenon: A comparison with neon, argon and krypton complexes

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ABSTRACT

H-bonding-like interactions between AH acids and Ne, Ar, Kr and Xe are examined by analysis of predicted A–H···Rg geometry, energy, A–H stretching vibration (CCSD(T) level) as well as assumed proton affinitiy, pKa, polarizability and chemical hardness of the complex components. The Kr and Xe systems are described as mostly the acid–base contacts and reveal properties of typical H-bonded complexes. These contacts are also influenced by structural factors. Properties of the Ne contacts are qualitatively different. The A–H···Xe complexes can be divided into stronger and weaker ones using the ^{129}Xe chemical shift as the criterion.

1. Introduction

Interactions between the noble atoms (Rg) and acids are important for two reasons. The first one is the biological activity of Rg, Xe especially [1–4], the second one is a fundamental role of very weak hydrogen bonding and van der Waals interactions in the matter organization ([5] and references herein).

The anesthetic efficiency of the noble gases decreases in the order: Xe, Kr, Ar, Ne, He. The Xe gas is very well known as excellent anesthetic [6], Kr and Ar are also anesthetics but not so efficient, Ne and He do not produce anesthesia [7]. This order obviously results from the chemical activity of the noble atoms – it has been known for a long time that a very weak association should play a key role in the general anesthesia [2]. This idea was confirmed recently by Liu and Tang by discovering structural and functional changes of *N*-methyl-D-aspartate receptor (NMDA) due to interactions between Xe and the NMDA H-bond network [3].

The distinction between very weak H-bonding interactions, both the blue-shifting and the red-shifting ones, and van der Waals interactions is not easy and can be controversial [8]. This problem was considered experimentally and theoretically in several papers (e.g. [5,9–11]. Also previous studies in our group were focused on these kinds of interactions [12,13].

Recently we have predicted (MP/2 level of theory) and analyzed ^{129}Xe shielding variations due to the A–H···Xe contacts in the H-bonding-like configuration, where AH are twelve BrØnsted acids of different chemical structure and acidity: FH (**1**), ClH (**2**), BrH (**3**), NCH (**4**), CNH (**5**), HOH (**6**), FOH (**7**), ClOH (**8**), BrOH (**9**), HCOOH (**10**), FCOOH (**11**), ClCOOH (**12**) [12]. In this Letter we intend to characterize the nature of the A–H···Xe dimers in relation to the analogical systems formed by lighter noble atoms (Rg), using a more advanced computational method (CCSD(T) level of theory). For this reason we consider four shorter series of the A–H···Rg systems (acids **1**–**9**) in the H-bonding-like configuration: A–H···Ne, A–H···Ar, A–H···Kr and A–H···Xe.

The aim of our work is to understand the role of the AH acidity, the Rg basicity and possibly H-bonding in the A–H···Rg contacts. This problem seems to be important in the relation to the general discussion on the nature of very weak interactions and particularly to the noble gases activity in the human body.

2. Methodology

2.1. Computational methods

The CCSD(T) level of theory has been used for both geometry optimization and energy calculations steps. Geometry optimization with def2-TZVPPD basis set was followed by single point energy calculation with def2-QZVPPD basis set [14]. In order to include possible relativistic effects arising from the presence of Xe atom, def2-ecp effective core potential has been put on this center [15]. The energy and gradient convergence criteria in the optimization step were set to 1×10^{-8} and 1×10^{-6} respectively. The same energy threshold was applied at single point energy calculations. To get rid of the basis set superposition error in values of calculated interaction energy, a counterpoise correction was applied [16,17]. Harmonic frequencies were calculated in order to determine whether an optimized structure is in an energy minimum with respect to its vibrational degrees of freedom.

All calculations were performed with Molpro 2010.1 [18] and Gaussian 2003 [19] codes. Basis sets were taken from EMSL Basis Set Library [20,21].

Results obtained for the Xe complexes are discussed in the relation to our recent predictions based on the MP2 level of theory [12].

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2.2. Analysis

Our considerations are based on several parameters:

1. PA(AH), assumed experimental proton affinities of the uncomplexed acids (in kJ mol^{-1}): 1553.5 (**1**), 1394.9 (**2**), 1353.5 (**3**), 1468.2 (**4**), 1633.0 (**6**), 1516.7 (**7**), 1487.8 (**8**), 1479.0 (**9**) [22]. PA(CNH): 1412.9 (**5**) was calculated [22].
2. PA(Rg), assumed proton affinities of the rare gas atoms (in kJ mol^{-1}): 201 (Ne), 371 (Ar), 425 (Kr), 496 (Xe) [23].
3. pKa, assumed p*K*a values of the AH acids dissolved in water: 3.2 (**1**), −7.0 (**2**), −9.0 (**3**), 9.2 (**4**), 14.0 (**6**), 7.4 (**8**), 8.6 (**9**) [24,25].
4. η(Rg), assumed chemical hardness of the Rg bases (in a.u.): 0.568 (Ne), 0.393 (Ar), 0.347 (Kr), 0.302 (Xe) [26].
5. $\eta(A^-)$, assumed chemical hardness of the A^- conjugate bases of the AH acids (in a.u.): 0.257 (F^-), 0.173 (Cl^-), 0.154 (Br^-), 0.195 (CN^-), 0.206 (HO^-), 0.165 (ClO^-) [27]. The chemical hardness for the remaining ions: 0.193 (FO^-) and 0.149 (BrO^-) was estimated from the $\eta(A^-) = ½[IP(A^-) - EA(A^-)]$ formula, where $IP(A^-)$ and $EA(A^-)$ are the ionization potential and electron affinity of considered ions (respectively; [27]), and were $IP(A^-) - EA(A^-) \approx IP(A) - EA(A)$ was assumed according to [28]. IP for the FO and BrO radicals was taken from [29] and [30], respectively, EA(FO) and EA(BrO) from [31].
6. α(Rg), assumed experimental ground state polarizabilities of the Rg atoms (in a.u.): 2.38 (Ne), 10.77 (Ar), 16.47 (Kr), 26.97 (Xe) [32].
7. ΔE, calculated interaction energy of the dimers including basis set superposition error corrections ($\Delta E'$) and zero-point vibrational energy corrections ($\Delta E = \Delta E' + ZPVE$) – this Letter.
8. $\Delta R = R(A\text{–}H\cdots Rg) - R(A\text{–}H)$, calculated variation of the A–H distance, due to the complexation – this Letter.
9. $\Delta\nu = \nu_c - \nu_a$, calculated (in harmonic approximation) variation of the A–H stretching vibration, due to the complexation, expressed in wavenumbers – this Letter.
10. $\Delta\lambda = \Delta\nu/\nu_c\nu_a = \nu_a^{-1} - \nu_c^{-1} = \lambda_a - \lambda_c$, calculated 'reduced $\Delta\nu$' expressed in wavelengths – this Letter.

Table 1

Calculated (at CCSD(T)/def2-TZVPPD level of theory) ΔE interaction energies including basis set superposition error and zero-point vibrational energy corrections, selected distances in the A–H···Rg complexes, $\Delta R = R_c(A\text{–}H) - R_a(A\text{–}H)$ differences for isolated acids (a) and their complexes (c), $\Delta\nu = \nu_c(A\text{–}H) - \nu_a(A\text{–}H)$ and $\Delta\lambda = \Delta\nu/\nu_a\nu_c = \lambda_a - \lambda_c$ stretching vibration differences in harmonic approximation, assumed $\Delta PA = PA(AH) - PA(Rg)$ proton affinities and $\Sigma\eta = \eta(Rg) + \eta(A^-)$ chemical hardness.

Rg	AH	ΔE (kJ/mol)	ΔR·(10^5 Å)	$R(Rg\cdots A)$ (Å)	$R(H\cdots Rg)$ (Å)	$\Delta\nu$ (cm^{-1})	$\Delta\lambda$·(10^8 cm)	ΔPA[a] (kJ/mol)	$\Sigma\eta$[b] a.u.
Part 1									
Ne	FH	0.379	7	3.299	2.380	1.2	7	1353.6	0.825
	ClH	−0.004	−5	3.905	2.629	3.2	36	1194.9	0.741
	BrH[c]	−0.560	−16	4.125	2.706	4.0	56	1153.4	0.722
	NCH	−0.515	−2	3.683	2.615	2.0	17	1268.1	0.763
	CNH	−0.939	12	3.425	2.427	−0.8	−6	1212.9	–
	HOH[d]	0.120	−7	3.386	2.597	1.5	10	1434.2	0.774
	FOH	−0.250	−2	3.347	3.495	3.2	23	1317.9	0.761
	ClOH	−0.339	−6	3.393	2.471	4.3	20	1289.0	0.733
	BrOH	−0.626	−7	3.419	2.478	4.8	33	1280.2	0.717
Ar	FH	0.159	71	3.487	2.567	−13.7	−80	1183.6	0.650
	ClH	−0.775	24	4.127	2.850	−0.6	−6	1024.9	0.566
	BrH	−1.637	1	4.346	2.926	2.7	38	983.4	0.547
	NCH	−1.419	27	3.960	2.892	−2.4	−20	1098.1	0.588
	CNH	−1.274	87	3.643	2.644	−16.	−110	1042.9	–
	HOH[e]	−0.552	13	3.527	3.061	−1.7	−27	1263.8	0.599
	FOH	−1.282	32	3.575	2.644	−2.2	−38	1147.5	0.586
	ClOH	−1.678	35	3.569	2.623	−2.8	−50	1118.6	0.558
	BrOH	−1.699	30	3.585	2.631	−1.8	−32	1109.8	0.542
Kr	FH	−0.220	113	3.613	2.692	−24.5	−144	1129.6	0.604
	ClH	−1.022	55	4.213	2.936	−5.5	−61	970.9	0.520
	BrH	−1.397	25	4.423	3.003	−0.7	−9	929.4	0.501
	NCH	−1.716	48	4.089	3.020	−5.8	−50	1044.1	0.542
	CNH	−2.566	130	3.373	2.784	−24.9	−172	988.9	–
	HOH	−0.509	25	3.881	2.928	−2.1	−13	1230.6	0.553
	FOH	−1.703	71	3.696	2.748	−10.2	−73	1114.3	0.540
	ClOH	−2.277	78	3.678	2.727	−11.9	−83	1085.4	0.512
	BrOH	−2.354	68	3.692	2.734	−10.2	−71	1076.6	0.496

Rg	AH	ΔE (kJ/mol)	ΔR·(10^5 Å)	$R(Rg\cdots A)$ (Å)	$R(H\cdots Rg)$ (Å)	$\Delta\nu$ (cm^{-1})	$\Delta\lambda$·(10^8 cm)	ΔPA[a] (kJ/mol)	$\Sigma\eta$[b] a.u.	δ(^{129}Xe) (ppm)[f]
Part 2. The additional values in the parenthesis are taken from Ref. [12] (MP2 level of theory)										
Xe	FH	−0.481 (−2.677)	164 (149)	3.791 (3.840)	2.871 (2.920)	−37.6 (−35.9)	−222 (−210)	1058.6	0.559	(60.07)
	ClH	−1.199 (−3.772)	108 (152)	4.254 (4.295)	3.077 (3.024)	−13.6 (−22.1)	−152 (−237)	899.9	0.475	(75.79)
	BrH	−1.568 (−4.070)	82 (153)	4.542 (4.445)	3.121 (3.035)	−7.8 (−18.3)	−111 (−245)	858.4	0.456	(84,83)
	NCH	−1.970 (−2.804)	75 (63)	4.253 (4.351)	3.184 (3.285)	−10.5 (−9.9)	−90 (−83)	973.1	0.497	(58.29)
	CNH	−2.507 (−3.916)	183 (154)	3.969 (4.002)	2.970 (3.004)	−35.9 (−32.6)	−250 (−224)	917.9	–	(65.42)
	HOH	−0.577 (−1.413)	47 (39)	4.039 (4.177)	3.084 (3.233)	−4.7 (−4.8)	−31 (−30)	1133.4	0.508	(62.85)
	FOH	−2.090 (−2.884)	126 (96)	3.865 (3.964)	2.905 (3.007)	−22.2 (−19.2)	−158 (−134)	1017.1	0.495	(57.72)
	ClOH	−2.898 (−4.240)	139 (123)	3.832 (3.891)	2.876 (2.946)	−25.6 (−25.5)	−179 (−178)	988.2	0.467	(54.40)
	BrOH	−3.011 (−4.767)	128 (119)	3.842 (3.896)	2.882 (2.947)	−23.6 (−24.9)	−165 (−173)	979.4	0.451	(54.37)

[a] Ref. [22,23].

[b] Ref. [26,27].

[c] Second order saddlepoint with respect to double degenerate mode at i11.77 cm^{-1}.

[d] Transition state (i19.47 cm^{-1}).

[e] Transition state (i7.06 cm^{-1}).

[f] The ^{129}Xe isotropic chemical shift of the A–H···Xe complexes [12].