Charge-Shift Bonding in Xenon Hydrides： An NBO/NRT Investigation on HXeY ··HX (Y = Cl, Br, I; X = OH, Cl, Br, I, CCH, CN) via H-Xe Blue-Shift Phenomena

Supporting Information

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Table S1. Calculated bond lengths $R_{H\text{-}Xe}$ and $R_{Xe\text{-}Y}$ (in Å) and monomer-to-complex frequency blue shifts (in cm^{-1}) of H-Xe stretching mode for hydrogen-bonded complexes HXeY ··HX (Y = Cl, Br, I; X = OH, Cl, Br, I, CN, CCH) as well as the angle (in °) between HXeY and HX in Structure A at the MP2/def2-TZVPPD level of theory, with available experimental blue shifts. The data in parentheses were calculated at the CCSD(T) level of theory.

Monomers/Complexes	$R_{H\text{-}Xe}$	$R_{Xe\text{-}Y}$	Angle(°)	H-Xe blue shifts	H-Xe blue shifts (exp)
HXeCl	1.666	2.616			
HXeCl ··H_2O	1.646	2.671	75	101 (118)[c]	82[c]
HXeCl ··HCl	1.645	2.672	82	103	116[d]
HXeCl ··HBr	1.644	2.674	82	102	
HXeCl ··HI	1.646	2.670	82	114	
HXeCl ··HCN	1.648	2.661	92	88	
HXeCl ··HCCH	1.655	2.642	79	51	
HXeBr	1.679	2.774			
HXeBr ··H_2O	1.656	2.825	71	116 (148)[c]	101[c]
HXeBr ··HCl	1.657	2.822	77	110	122[d]
HXeBr ··HBr	1.656	2.823	77	110	149[d]
HXeBr ··HI	1.658	2.819	78	90	
HXeBr ··HCN	1.658	2.817	88	106	
HXeBr ··HCCH	1.667	2.798	75	58	
HXeI	1.708	2.976			
HXeI ··H_2O	1.679	3.022	67	139 (188)[c]	138[c]
HXeI ··HCl	1.682	3.017	72	122 (167)[b]	94, 111, 155[b]
HXeI ··HBr	1.681	3.017	72	122 (149)[a]	110, 157[a]
HXeI ··HI	1.683	3.012	72	107 (120)[a]	75, 96[a]
HXeI ··HCN	1.680	3.015	83	132	
HXeI ··HCCH	1.693	2.996	70	67 (104)[b]	49, 55[b]

[a] From ref. Tsuge et al., 2013.

[b] From ref. Zhu et al., 2015.

[c] From ref. Tsuge et al., 2014.

[d] From ref. Lignell et al., 2008.

Table S2. Second-order perturbation energies($E^{(2)}$, kcal·mol^{-1}) due to donor-acceptor interactions in HXeY at the MP2/def2-TZVPPD level of theory.

Molecules	$n_Y \rightarrow \sigma^*_{H\text{-}Xe}$	$n_H \rightarrow \sigma^*_{Xe\text{-}Y}$	$n_{Xe} \rightarrow \hat{\sigma}^*_{H\text{-}Y}$
HXeCl	64.57	3957.00	1363.55
HXeBr	65.75	5187.90	1102.19
HXeI	70.75	5125.55	845.16

Explanation of the Procedure Employed to Calculate the BO of the Xe-H Bond

1. Conceptual Model in NBO/NRT

In the NBO/NRT framework, the fundamental starting point for a rational electronic theory of bonding is the Lewis-structure representation of the shared and unshared electrons in each atomic valence configuration, as formulated by Lewis. Based on the Lewis-structure model, perturbation theory is used to calculate systematically the corrections that bring the Lewis-structure model into an improved Lewis-structure model. In NBO/NRT language, it is the natural Lewis-structure model.

Subsequently, bonding analysis can be dissected into localized and delocalized contributions.

Take HXeY as an illustrative example. HXeY could be described as the hybrid of three resonance structures: H-Xe^{+} Y^{-}, H:$^{-}$ Xe^{+}-Y, and H^Y. When we focus on the H-Xe bond, the structure Ⅰ provides a localized contribution due to electron-sharing bonding. In structure Ⅱ, it is a delocalized contribution arising from a donor-acceptor interaction. In chemical language, it is dative bonding. Structure Ⅲ is a long-bonding structure. There is no contribution to the H-Xe bond strength, because there are neither localized contributions nor delocalized contributions to the H-Xe bonding.

2. Calculate the Weighting of Resonance Structure

A quantitative resonance theory can help us to find the weighting of resonance structure α, according to

D(true) = $\sum_{\alpha} \omega\alpha D\alpha^{(L)}$

where D(true) is the true density matrix of the system of interest. $D\alpha^{(L)}$ is corresponding to the density matrix of the resonance structure α. Note that $\sum_{\alpha} \omega\alpha=1$.

3. Calculate Each Property of the System

In the NRT of framework, each property <P>true of the true delocalized system can be represented in resonance-averaged form

<P>true = $\sum_{\alpha} \omega\alpha < P > \alpha$

where <P>α is the value of the property for natural resonance structure α.

Still take HXeY as an example. The H-Xe bond strength D(H-Xe) can be written as $D(H\text{-}Xe) = \omega_I D_I + \omega_{II} D_{II} + \omega_{III} D_{III}$.

From the conceptual analysis of the natural Lewis-structure, we know $D_{III} = 0$. Thus, $D(H\text{-}Xe) = \omega_I D_I + \omega_{II} D_{II}$

4. Calculate Bond Order of H-Xe

When using the bond order to reflect the H-Xe bond strength, D_I and D_{II} can be written as $D_I = k_I \omega_I b_I$, $D_{II} = k_{II} \omega_{II} b_{II}$, where b_I represents the normal covalent H-Xe bond order in resonance structure Ⅰ, b_{II} is the H-Xe dative bond order in resonance structure Ⅱ.

If $k_I = k_{II} = k$, and $b_I = b_{II} = 1$, we obtain $b(H\text{-}Xe) = \omega_I + \omega_{II}$ for our studied HXeY.

It is worthwhile noting that the present NBO/NRT methods could not provide the ratio of k_I / k_{II}, and that the adequacy in calculating the BO of the H-Xe bond has been tested through indirect comparisons with experimental results.