A Comparative Computational Study on the Hydrogen Adsorption on the Ag^+, Cu^+, Mg^{2+}, Cd^{2+}, and Zn^{2+} Cationic Sites in Zeolites

Paweł Kozyra, Witold Piskorz
Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

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Supporting Information

Interaction Cu(II) site with hydrogen

In the copper containing zeolites some Cu^{2+} cations undergo autoreduction forming Cu^+ cations while the rest of them remain in the original oxidation state and both constitute adsorption centres for hydrogen. For that reason, even though the Cu^{2+} cation, having d^9 configuration, is the open-shell system, contrary to those discussed in this article, we have performed analogous computation. For the Cu^{2+} cation, despite it having unpaired electron, the spin density does not change upon interaction with hydrogen molecule and this interaction resembles that for Mg(II), Cd(II), and Zn(II).

The distances between the hydrogen molecule and the Cu^{2+} cation are close to those for Zn^{2+} so are the coordination numbers for respective structures, see Table 2. Moreover, the interaction energy values and the extent of the H-H bond activation (measured by the red-shifts, $\Delta\nu$, and H-H elongations, Δr_{HH}) are similar for these two cations (Table 2). The calculations for the $[(M7)CuH_2]^0$ model show that the Cu^{2+} cation is not stable while two-coordinated, contrary to Zn^{2+}. Hence, the H_2 molecule, bound to the cation, is unable to approach the framework oxygens when it could have interacted with them, as it is in case of Zn^{2+}. Comparing to Cu^+, for Cu^{2+} the π-backdonation is negligible. Since the fourfold coordination is stable, the Cu^{2+} charge is neutralised to the large extent so that the σ-donation is not able to activate H-H strongly enough.

The conclusion of the $\Delta\nu$ *vs.* Δr_{HH} correlation has been positively verified by the Cu^{2+}cation (Fig. 2).

As the systems containing Cu^{2+} cation: $[CuH_2]^{2+}$, $[(T1)CuH_2]^+$, and $[(M7)CuH_2]^0$, are open-shell, the spin-resolved NOCV analysis has been performed for α and β electrons independently. Only the σ-donation and the σ-backdonation contributions were significant (Table 3), similarly as for the Mg^{2+}, Cd^{2+}, and Zn^{2+} sites. Also, the contours of contribution to deformation density form a similar picture (Fig. 3).

Moreover, even though the systems with the Cu^{2+} cation, specifically demanding for its electronic structure significantly different from those for which the model has been optimized (d^{10} cations), were not included in determining the Δr_{HH}^{NOCV} *vs.* Δr_{HH} dependency (calculated according to Eq. 2, see Fig. 4), they match that dependency. Hence, the Cu^{2+} systems fit, in the same way, the Δr_{HH} *vs.* ΔE_{orb}^{i} dependency, so the either said relationship seems quite universal one.

References

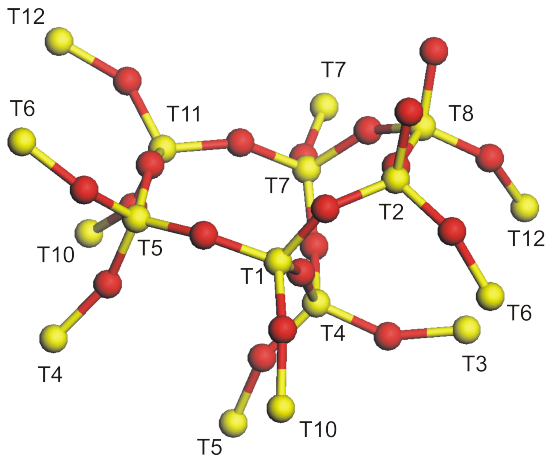

Figure 1 Naming of T positions in M7 model, after[?]

Table 1 Energy changes between given elementary step and the previous step ($\Delta E'$) without (DFT) or with dispersion (DFT+D), (ΔE_{D}), energy changes due to the DFT+D reoptimization (ΔE_{opt}).

Structure	Label, n	$\Delta E' = E_n - E_{n-1}$ /(kcal · mol^{-1})		$\Delta E_{\mathrm{D}} =$	$\Delta E_{\mathrm{opt}} =$
		E_{DFT}	$E_{\mathrm{DFT+D}}$	$(E_{\mathrm{DFT+D}} - E_{\mathrm{DFT}})$ /(kcal · mol^{-1})	$\left(E^{\mathrm{geom.opt.}}_{\mathrm{DFT+D}} - E^{\mathrm{SCF}}_{\mathrm{DFT+D}}\right)$ /(kcal · mol^{-1})
[(M9)Zn]* + H_2	**1**	–	–	–	−0.3
[(M9)ZnH_2]	**2**	−41.4	−45.5	−4.1	−0.3
$TS_{2,4}$	**3**	35.0	35.4	0.4	−0.1
[(M9)ZnHH]	**4**	−7.8	−8.3	−0.5	−0.2
$TS_{4,6}$	**5**	20.1	20.0	−0.1	−0.2
[(M9)HZnH]	**6**	−53.9	−51.1	2.8	−0.4
[(M9)Zn]* + H_2	**8**	46.1	47.7	1.6	−0.2

Table 2 The measure of H-H bond activation – Δr_{HH}, $\Delta\nu$, and $\Delta E_{\mathrm{total}}$, for the systems with Cu^{2+} cation.

Model label	Model	Coord number	r_{MH} /Å	Δr_{HH} /pm	$\Delta\nu$ /cm^{-1}	$\Delta E_{\mathrm{total}}$ /kcal · mol^{-1}
r	$[CuH_2]^{2+}$	0	1.85	8.8	−1072	−50.5
s	$[(T1)CuH_2]^{+}$	2	1.88	2.9	−415	−13.2
t	$[(M7)CuH_2]^{0}$	4	2.14	1.2	−177	−3.5

Table 3 Elongation of H-H bond (Δr_{HH}), sum of orbital interaction energies (ΔE_{orb}) for α and β electrons, its contributions: σ-donation ($\Delta E^{\mathrm{don}}_{\mathrm{orb}}$) and respective NOCV charge transfer estimates (λ^i) for the systems with Cu^{2+} cation.

Model	Coordi-nate number	Δr_{HH}/ pm	ΔE_{orb}/ kcal · mol^{-1}	σ-donation ($\alpha+\beta$)		σ-donation		σ-donation	
				$\Delta E^{\mathrm{don}}_{\mathrm{orb}}$	λ^{don}	$\Delta E^{\mathrm{don}}_{\mathrm{orb}}$ (α)	$\Delta E^{\mathrm{don}}_{\mathrm{orb}}$ (β)	λ^{bdon} (α)	λ^{bdon} (β)
$[CuH_2]^{2+}$	0	8.8	−45.1	−41.3	0.49	−21.0	−20.3	0.25	0.24
$[(T1)CuH_2]^{+}$	2	2.9	−20.0	−13.5	0.27	−6.9	−6.6	0.14	0.13
				−1.1*	0.05*		−1.1*		0.05*
$[(M7)CuH_2]^{0}$	4	1.2	−11.9	−5.3	0.20	−2.7	−2.6	0.10	0.09

*– σ-backdonation

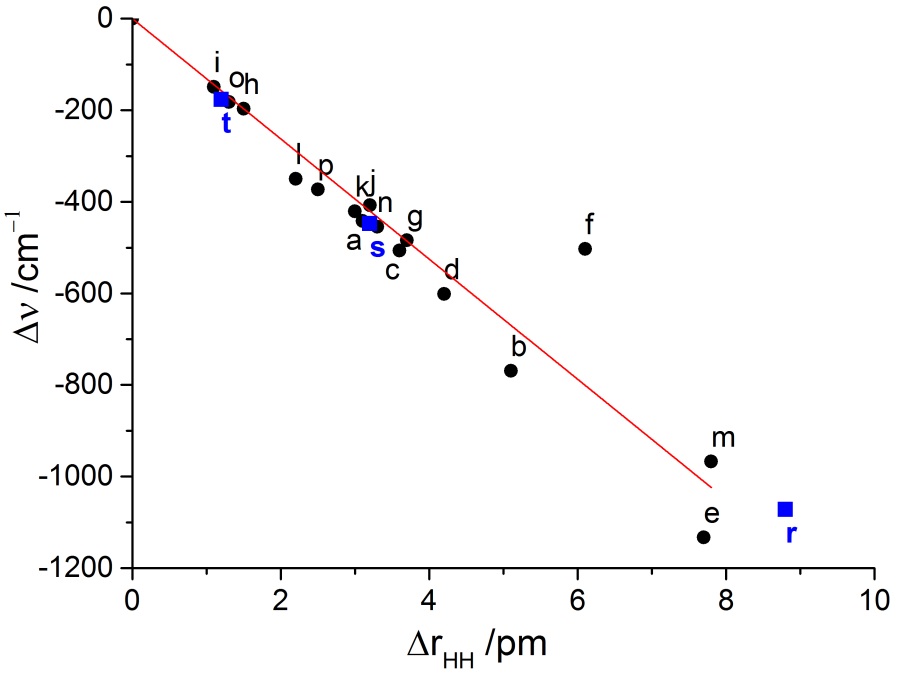

Figure 2 Correlation between H-H bond elongation (Δr_{HH}) and IR red-shift ($\Delta \nu_{HH}$) cationic MFI sites. Labelling refers to Table 2.

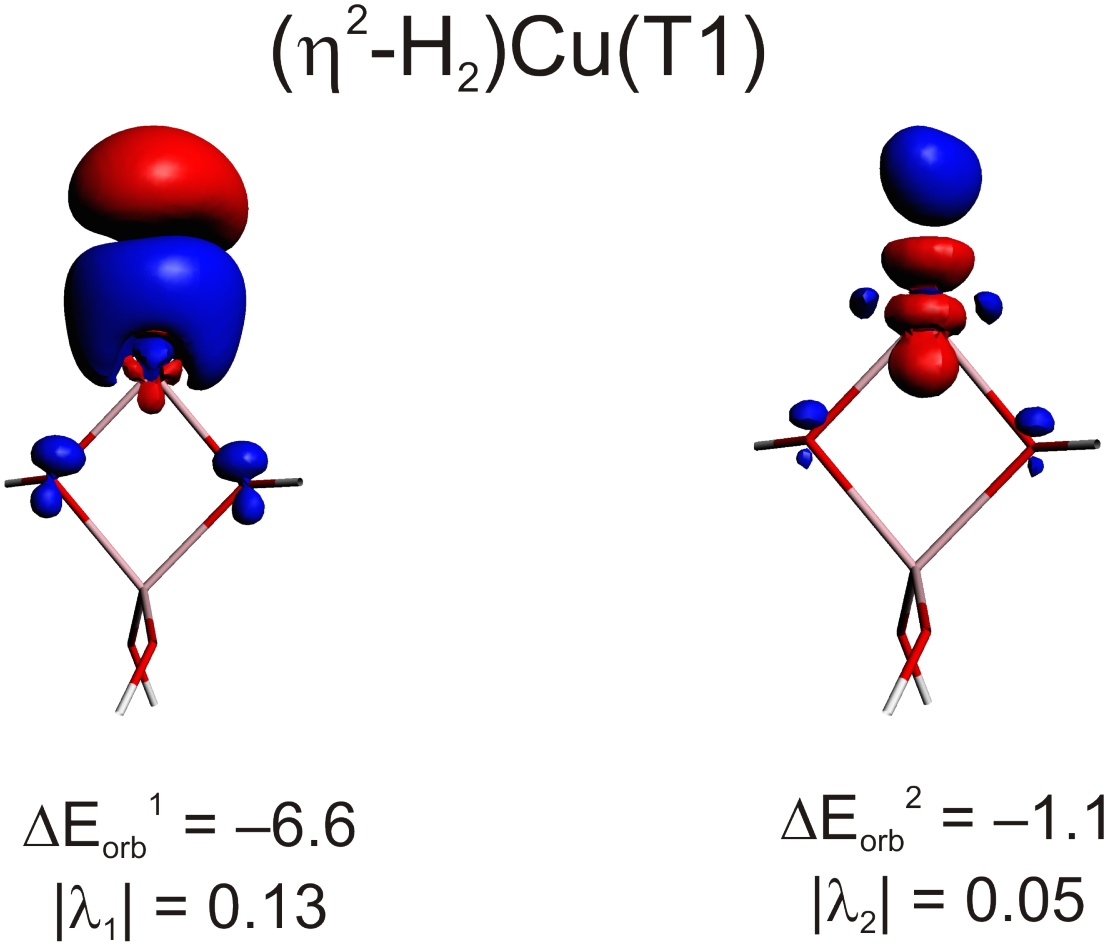

Figure 3 Contributions to deformation β electron density for $[(T1)ZnH_2]^+$ together with the corresponding orbital interaction energy contributions (ΔE^i_{orb}/kcal $\cdot$ mol^{-1}) and NOCV charge transfer estimates (λ_i). Red (light grey) – density outflow, blue (dark grey) – density inflow (contour value 0.001 a.u., colour figures on-line).

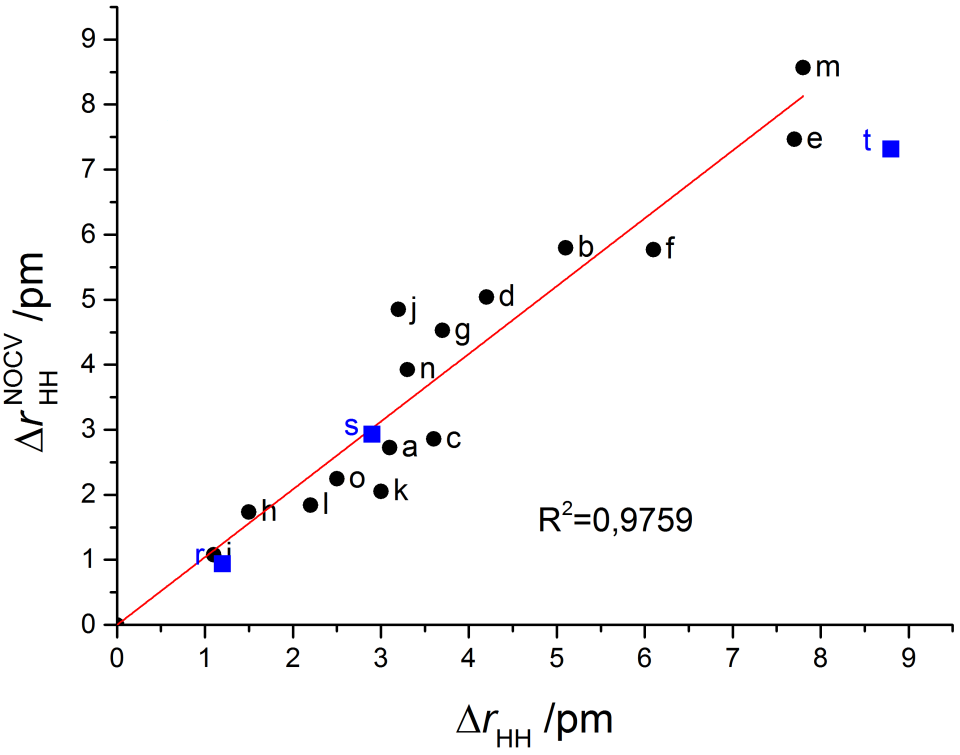

Figure 4 H-H bond elongation calculated from contributions to orbital interaction energy (Δr_{HH}^{NOCV}) *vs.* calculated wave numbers (Δr). Labelling refers to Table 2.