Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

for

Improving Alkane Dehydrogenation Activity on γ-Al_2O_3 through Ga Doping

Mona Abdelgaid, James Dean and Giannis Mpourmpakis

Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA

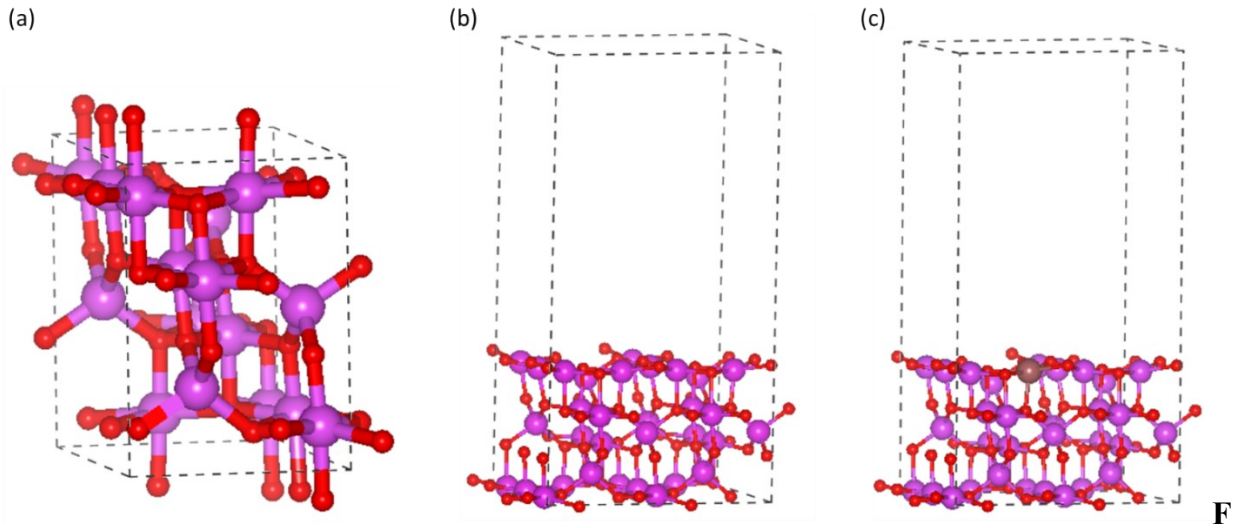

Figure S1. Structures of γ-Al_2O_3 (a) unit cell (b) super cell of 1×2 primitive cells of undoped (100) γ-Al_2O_3 c) super cell of 1×2 primitive cells of Ga^{Va}-doped (100) γ-Al_2O_3. O, Al, and Ga atoms are shown in red, purple, and brown, respectively**.**

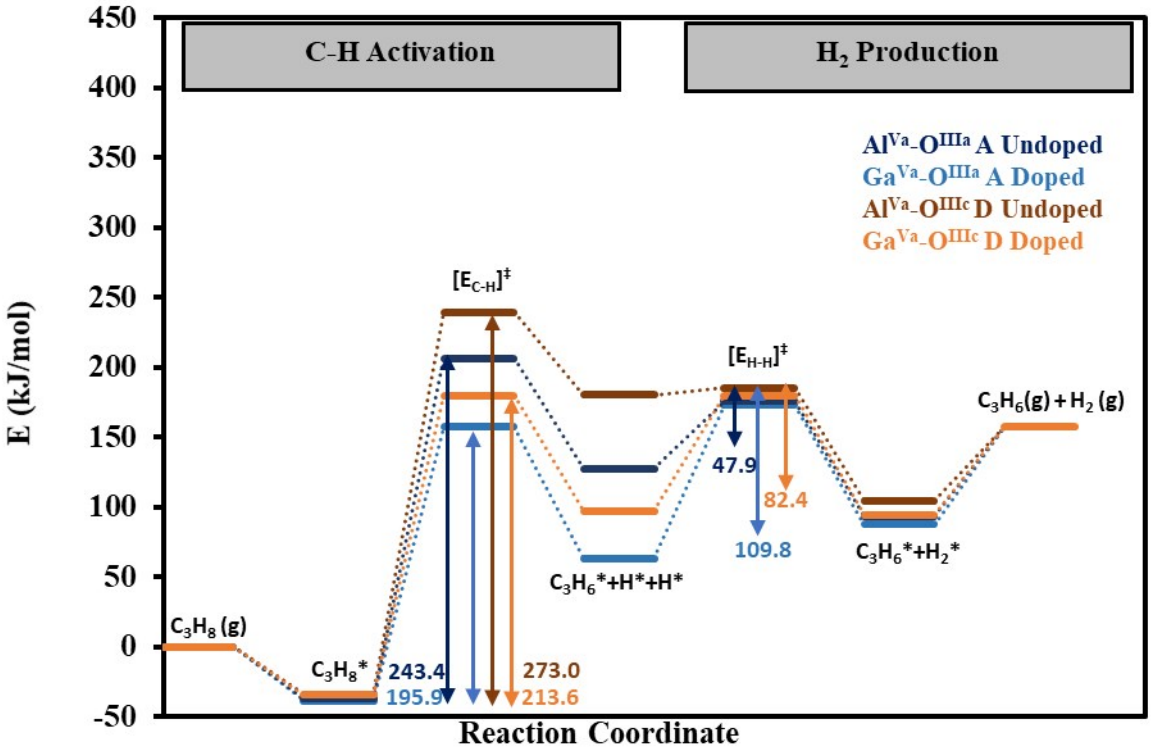

Figure S2. Reaction energy profile of propane dehydrogenation (PDH) on Ga^{Va}-doped and undoped (100) γ-Al_2O_3 via the concerted mechanism at the corresponding Lewis acid-base site pairs. $E^{‡}_{C\text{-}H}$ is the electronic energy of the transition state (TS) for C-H activation, whereas $E^{‡}_{H\text{-}H}$ is the electronic energy of the TS for hydrogen production. Adsorbed states are denoted with asterisks.

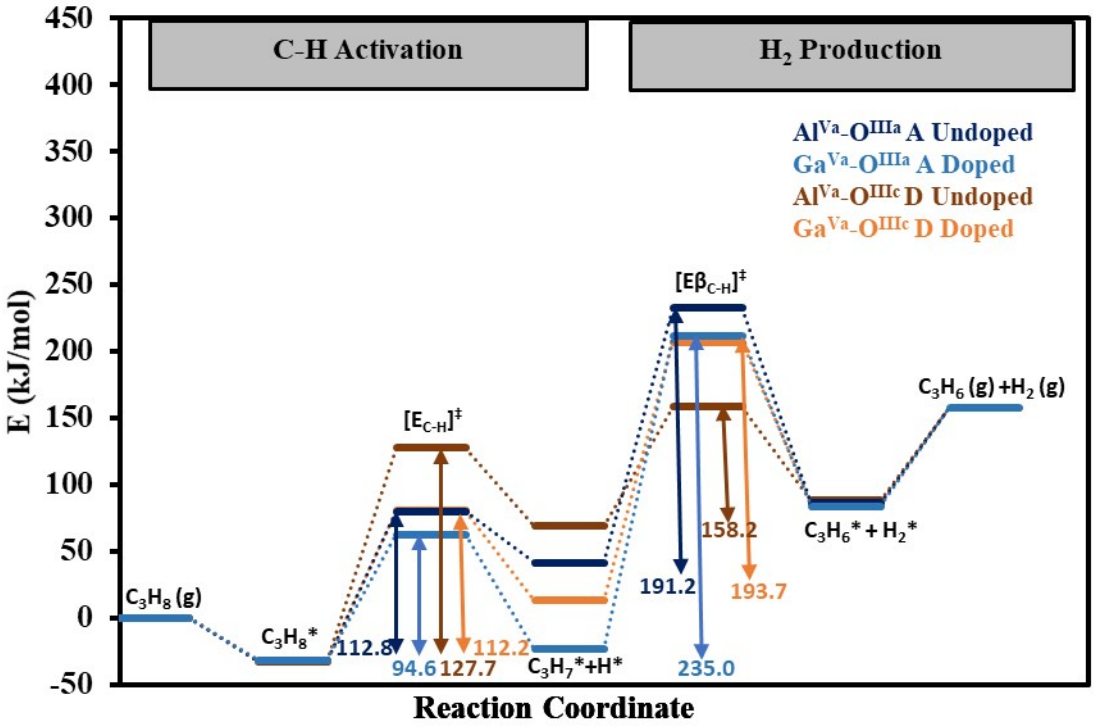

Figure S3. Reaction energy profile of propane dehydrogenation (PDH) on Ga^{Va}-doped and undoped (100) γ-Al_2O_3 via the stepwise mechanism at the corresponding Lewis acid-base site pairs. $E^{\ddagger}_{C\text{-}H}$ is the electronic energy of the TS for C-H activation, whereas $E^{\ddagger}_{\beta C\text{-}H}$ is the electronic energy of the TS for hydrogen production. Adsorbed states are denoted with asterisks.

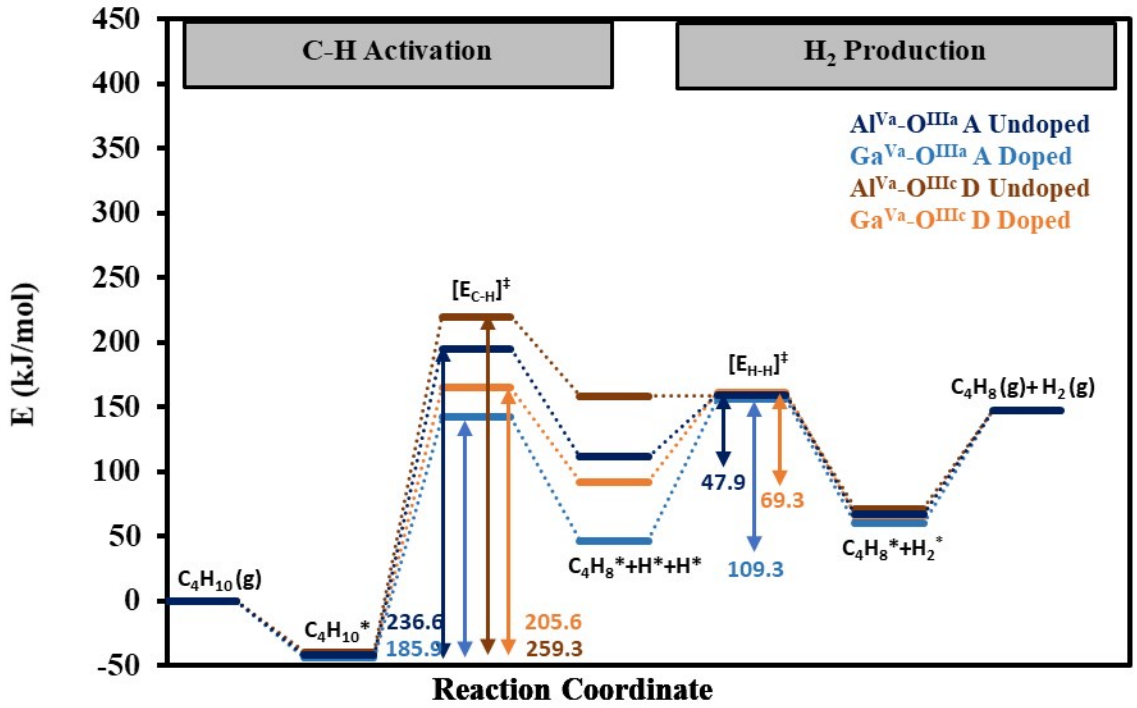

Figure S4. Reaction energy profile of isobutane dehydrogenation (i-BDH) on Ga^{Va}-doped and undoped (100) γ-Al_2O_3 via the concerted mechanism at the corresponding Lewis acid-base site pairs. $E^{‡}_{C\text{-}H}$ is the electronic energy of the TS for C-H activation, whereas $E^{‡}_{H\text{-}H}$ is the electronic energy of the TS for hydrogen production. Adsorbed states are denoted with asterisks.

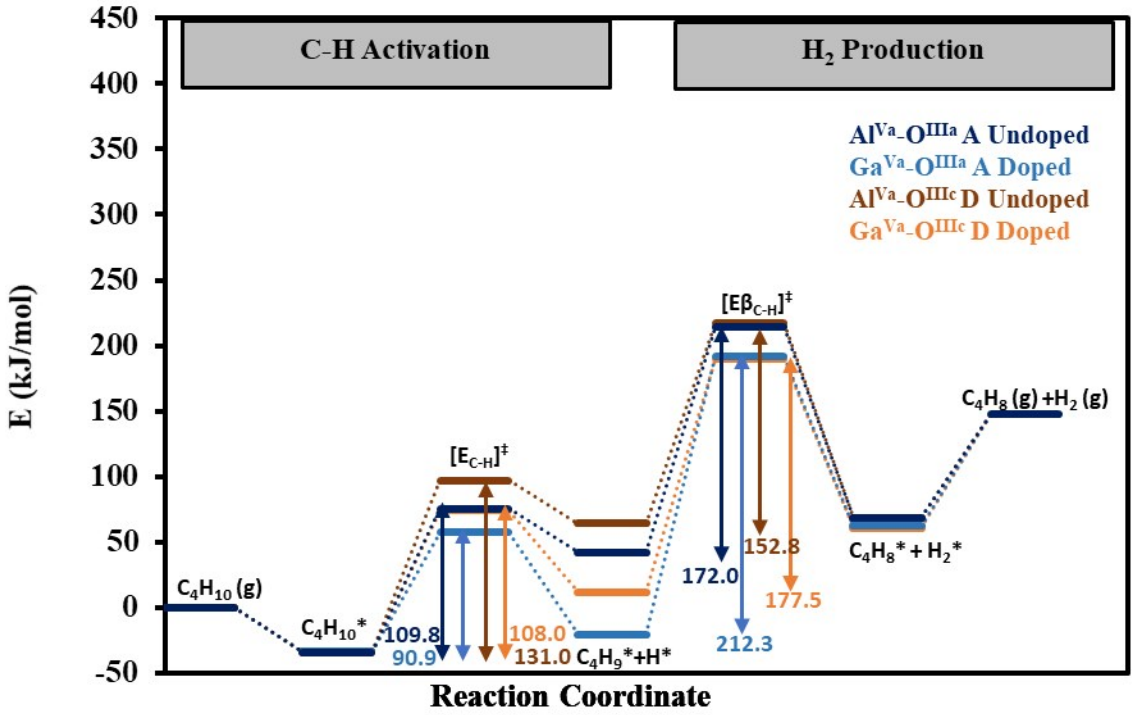

Figure S5. Reaction energy profile of isobutane dehydrogenation (i-BDH) on Ga^{Va}-doped and undoped (100) γ-Al_2O_3 via the stepwise mechanism at the corresponding Lewis acid-base site pairs. $E^{‡}_{C\text{-}H}$ is the electronic energy of the TS for C-H activation, whereas $E^{‡}_{\beta C\text{-}H}$ is the electronic energy of the TS for hydrogen production. Adsorbed states are denoted with asterisks.

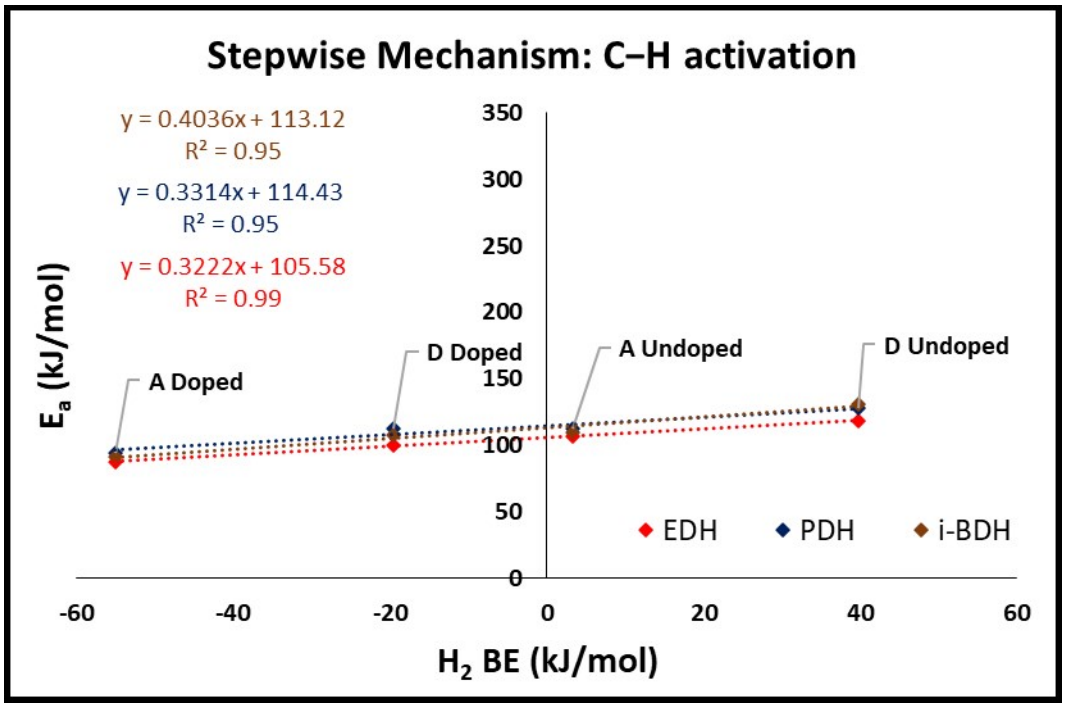

Figure S6. C-H activation barriers for the stepwise mechanism on Ga^{Va}-doped and undoped (100) γ-Al_2O_3 vs. H_2 BE on the corresponding Lewis acid-base site pairs. Red, blue, and brown diamonds correspond to ethane – EDH, propane – PDH, and isobutane – i-BDH dehydrogenation, respectively.

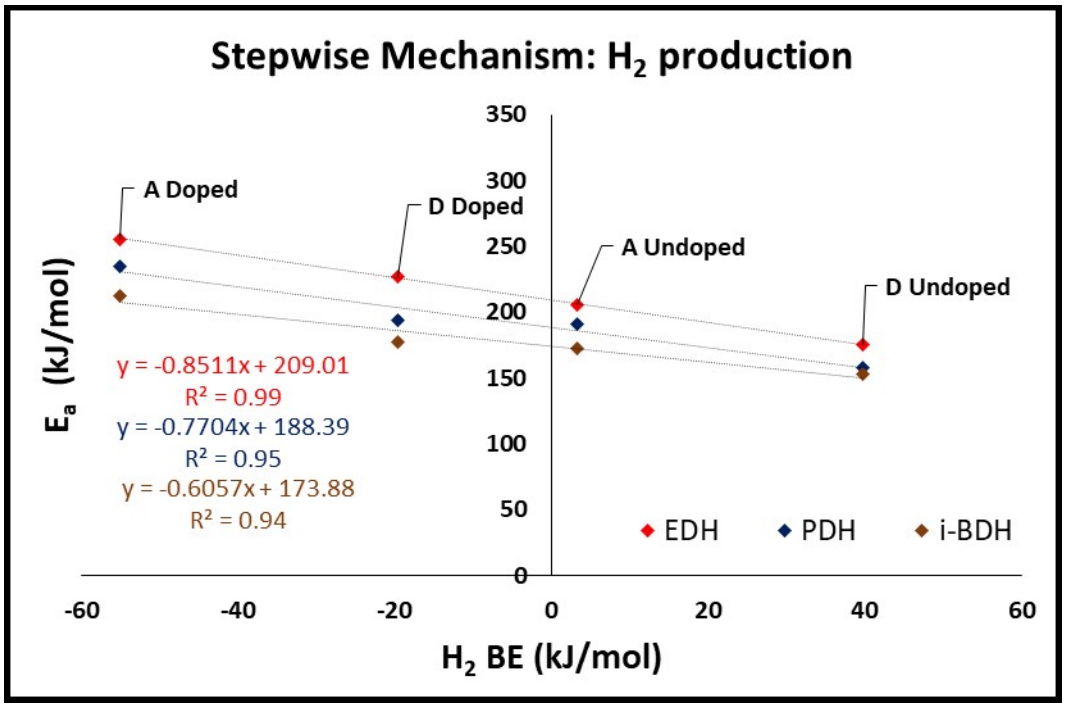

Figure S7. H_2 production barriers for the stepwise mechanism on (100) Ga^{Va}-doped and undoped γ-Al_2O_3 vs. H_2 BE on the corresponding Lewis acid-base site pairs. Red, blue, and brown diamonds correspond to ethane – EDH, propane – PDH, and isobutane – i-BDH dehydrogenation, respectively.

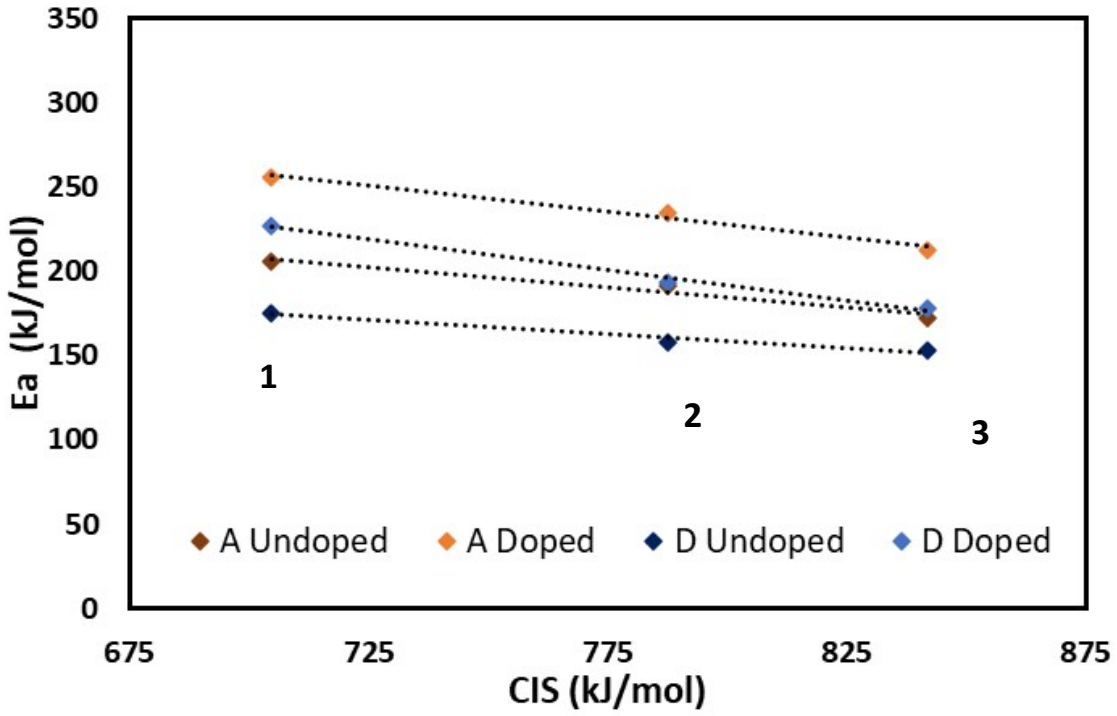

Figure S8. DFT-calculated H_2 production barriers vs. CIS for the stepwise mechanism at the respective acid-base site pairs. Data points corresponding to primary, secondary, and tertiary carbocation intermediates are denoted with numerical insets (primary: 1, secondary: 2, tertiary: 3).

Table S1. Alkane dehydrogenation model parameters and standard error associated with data regression for the concerted mechanism. Fitted values resulted in a R^2 value of 0.9807

	Parameter	**Std Error**
Intercept	375.9	20.28
H_2 BE	0.861	0.042
CIS	-0.175	0.026

Table S2. Alkane dehydrogenation model parameters and standard error associated with data regression for the stepwise mechanism. Fitted values resulted in a R^2 value of 0.9639

	Parameter	**Std Error**
Intercept	400.105	26.55
H_2 BE	-0.7424	0.055
CIS	-0.2695	0.034

Table S3. Values of turnover frequency (TOF)-determining transition state (TDTS) and TOF-determining intermediate (TDI) of ethane dehydrogenation (EDH), propane dehydrogenation (PDH), and isobutane dehydrogenation (i-BDH) on different site pairs of γ-Al_2O_3.

ADH reaction	Site pair	TDI (kJ mol^{-1})		TSTS (kJ mol^{-1})	
		Concerted	Stepwise	Concerted	Stepwise
EDH	A Undoped	-27.57	-27.47	227.27	250.82
	A Doped	-27.59	-26.20	178.35	235.73
	D Undoped	-27.79	-28.37	264.30	249.69
	D Doped	-29.54	-26.66	200.70	236.42
PDH	A Undoped	-36.73	-32.82	206.42	232.38
	A Doped	-38.42	-31.89	155.45	211.40
	D Undoped	-33.50	-32.52	239.50	227.00
	D Doped	-34.03	-32.00	179.60	206.84
i-BDH	A Undoped	-41.80	-34.32	194.81	214.33
	A Doped	-43.90	-33.63	142.0	191.67
	D Undoped	-39.50	-33.96	219.80	216.90
	D Doped	-40.80	-33.92	164.70	189.45