Supporting information

I. CO adsorption on (111) metals

Table 1. Physical characteristics of CO adsorption on Ni(111) [a]

site	E_{ads}	x_{0A}(M-CO)	h(C-O)	ω_A(M-CO)	ω(C-O)	References
	-31±0.7					Calorimetry [1]; $\theta \rightarrow 0$
3f-hollow brg		1.05±0.17 1.27	1.19±0.06			SEXAFS[2]; θ=0.5
	-30±2.5					TPD [3]; $\theta \rightarrow 0$
top brg fcc hcp	-35.7 -41.5 -43.8 -44.5	1.837 1.439 1.337 1.321	1.161 1.183 1.191 1.192		2037 1864 1805 1800	periodic DFT; GGA; θ=1/4 [4]
hollow top	-43.8 to -45	1.329	1.192	353 430	1804 2041	DFT/GGA/PW91[5] ; θ=1/4
fcc/hcp		(1.25/1.3)±0.04				photo-electron diffract.; θ=1/4 [6]
top brg		1.80±0.04 1.27±0.05	1.13 1.13			photo-electron diffract [7]
fcc hcp		(1.27 to 1.32) ±.1 1.29±0.07				photo-electron diffract ; θ=0.25 [8]
fcc hcp		1.29 ±0.07 1. 34±0.07	1.18±0.07 1.15±0.07			LEED; θ=1/2 ML [9]
	-30.0 -26.5 -23.5					LEED [10]; $\theta \rightarrow 0$ θ=0.1 to 0.3 θ=0.3 to 0.45
top brg				400	2050 1810	EELS; low coverage [11]
3f-hollow					1793 to 1822	FT-RAIRS; low θ [12]
top	-26					LEED;TDS [13]; θ=1/3
3f-hollow 2f -hollow top					1817 1910 2045	LEED; TDS [14] θ=0.05 θ=0.5 θ=0.57

Continue of Table 1

site	E_{ads}	x_{0A}(M-CO)	h(C-O)	ω_A(M-CO)	ω(C-O)	References
	-29.9					HREELS, $\theta \rightarrow 0$ [15]
brg				380	1815	EELS; θ=0.5 [16]
3f- hollow				400 to 410		EELS; low coverage [17]
	-27					UBI-QEP [18]
top brg hollow	–31.6 to –34.1 – 34.1 to –38.5 –35.7 to –40					Periodic DFT; GGA; θ =1/3 [19]

[a] Distances x_{0A} and h in Angstrøm , frequencies in cm^{-1}, CO adsorption energy (E_{ads}) in kcal/mol, θ is the surface covering;

Table 2 Physical characteristics of CO adsorption on Pt(111) [a]

site	E_{ads}	x_{0A}(M-CO)	h(C-O)	ω_A(M-CO)	ω(C-O)	References
	-32					theoret. BOC MP [18]
	-45 to -24					TPS;AES, LEED [13] θ= 0.027 to 0.5
top	-34.7±4			480	2100	LEED, EELS, TDS; low θ [20]
brg				380	1850	
top		1.85	1.15			LEED, $\theta \rightarrow 0$ [21]
brg		1.55	1.15			
top	-33.7/-37.8	1.87/1.86	1.16/1.15			DFT; B3LYP/PW91;θ =1/3 [22]
brg	-31.8/-38.6	1.49/1.46	1.18/1.17			
fcc	-32.3/-40.1	1.37/1.33	1.19/1.18			
hcp	-31/-39.6	1.38/1.35	1.19/1.18			
top	-30.9 to -38.5	2.00	1.157	487	2081	DFT/GGA;PW91; θ=1/4 [5]
brg				372	1880	
hollow				352	1793	
top				464		RAIRS; θ=0.5 [23]
brg				376		
top					2093	RAIRS; θ=0.1 [24]
brg					1871	
	-33.0±2					Ref 25; $\theta \rightarrow 0$ and θ=1/3
	-27.0±2					θ=0.5
terrace	-24 to -27					TDS [26]
step	-33					
	-29.6					AES; flash desorption mass Spectroscopy; θ~0 [27]
	-33.3					TDS; extrapol. to θ~0 [28]
top	-37.8	1.85	1.15			periodic DFT;LDA/GGA θ=1/2 [29]
	-29.9					Molec. scatt.; AES; LEED [30]
	-32±2					LITD [31]; low θ
top	-27±3.6				2083	SFG [32]; θ=1/2

Continue of table 2

site	E_{ads}	x_{0A}(M-CO)	h(C-O)	ω_A(M-CO)	ω(C-O)	References
				480		Refs 33-35
top brg				480	2090 1860	EELS; low θ high θ [36]
	-30 to -32					HEERL; low coverage [37]
top hollow	-26.5 -27.7	1.90 1.52	1.154 1.191		1987 1714	DFT; cluster model [38]; (7/6) (6/7)
	-43±2 -28±4.5					calorimetry [39]; θ→0 θ=0.5
top hollow	-19.1 to –32.7 -23.5 to –27.4					Periodic DFT[19]; θ=1/3
	-32					UBI-QEP [18]
top	-38.7	1.84	1.16			Periodic DFT; RPBE+AER; θ=1/4 [87]
top	-35.7	1.85	1.14			Periodic DFT; LDA; GGA; θ=1/4 [53]
top	-36.7					Periodic DFT; GGA; θ=1/4 [42]

[a] see footnote to Table 1

Table 3 Physical characteristics of CO adsorption on Pd(111) [a]

site	E_{ads}	x_{0A}(M-CO)	h(C-O)	ω_A(M-CO)	ω(C-O)	References
	-35.5 -28.5					TDS, LEED [45]; $\theta \rightarrow 0$ θ= 1/3
top brg 3f hollow	-30				2110 1962 1895	TPD; IRAS [46]; $\theta \rightarrow 0$
fcc hollow		1.29±.05	1.15±.05			LEED [47]; θ= 1/3
top brg fcc				 322	2097 1951 1893	RAIRS; HEERLS [48]; θ=0.72
fcc hollow hcp fcc		1.27±.05 1.37±.06 1.31±.06	 1.14±0.12 1.14±0.14			HRLEES [41]; θ= 1/3 θ= 0.5 θ= 0.5
hollow brg top					1823 1936 2092	RAIRS [50]; $\theta \rightarrow 0$ θ= 0.5 θ>0.5
	-33.5					Ref 51; low coverage
top brg fcc					2103 1950 1890	SFG [52]; θ>0.6 θ~0.6 θ~0.75
hollow						periodic DFT [5]; GGA; θ=1/3
	-48.2 to -49.3 -38.7	1.31	1.188	319	1810	PW91; RPBE
fcc hollow	-31.1		1.19			Periodic DFT; RPBE+AER; θ=1/4 [87]
	-34					UBI-QEP [18]
						DFT; cluster model [38];
top hollow	-21 -26.5	1.96 1.61	1.16 1.176		2012 1795	(7/6) (6/7)
top hollow	-23.5 to –28.1 -32.7 to –34.8					periodic DFT [19]; θ=1/3

[a] see footnote to table 1

Table 4. Physical characteristics of CO adsorption on Rh(111) [a]

site	E_{ads}	x_{0A}	h(C-O)	ω_A(M-CO)	ω(C-O)	References
top brg hcp fcc	-42.8/ -36.0 -41.7/ -32.4 -44.6/ -33.9 -42.1/ -31.8			466/463 346 344/346 339	2015/ 2027 1833 1758/ 1785 1777	periodic DFT; GGA/(GGA+U) θ=1/4 [54]
top	-42.9/ -35.7	1.99	1.162	468	2029	DFT;GGA: PW91/RPBE $\theta \rightarrow 1/4$ [5]
top	-34.6 -30					photoemission [55]; θ=0.18 θ=1/3
top	-38.5±1.4 -39.4±0.6					TREELS [56], θ=1/3: modulated beam single beam
top	-32.3					He [57]; θ= 1/3
top brg hcp fcc	-47/-38.7 -44/-36.6 -45.9/-35.5 -43.6/-33.4	1.83 1.50 1.41 1.37	1.17			periodic DFT [58] GGA; PW91/RPBE θ= 1/3
top		1.87±0.04	1.20±0.05			LEED; θ= 1/3 [59]
top hollow					2049 1831	HREELS; low coverage [60]
	-31.6					LEED; $\theta \rightarrow 0$ [61]
top top brg				480 400	1990 2070 1870	HREELS [62]; θ-->0 θ= 1/2
	-31					LEED, θ= 1/3 [63]
top hollow	-33.7 -31.4	1.86 147	1.162 1.182		1950 1687	DFT; cluster model [38]; (7/3) (6/7/3)
	-32					UBI-QEP [18]
top brg hollow					2025→20751 1875 1851	RAIRS, TDS [83] θ=0.08→0.78 θ=0.64 to 0.78 θ=0.64 to 0.78

Continue of Table 4

top	-43.8	1.845	1.163	507	2003	Periodic DFT-GGA [83] θ=1/8
brg	-46.1					$\theta \to 0$
fcc	-47.7					-“-
hcp	-49.6					-“-
top	-39.4	1.86	1.17			Periodic DFT; RPBE+AER; θ=1/4 [87]
brg	-36.0	2.04				
fcc	-36.2	2.13				
hcp	-37.6	2.11				
top	-37.1±1			468	2015	HREELS,TDS,LEED [85] low θ~0
hollow				390	1861	θ>1/3
top					2020 to 2060	DFT, (9/4) cluster model [86]
hollow					1795 to 1862	

[a] see footnote to Table 1

Table 5 Physical characteristics of CO adsorption on Ir(111) [a]

site	E_{ads}	x_{0A}	h(C-O)	ω_A(M-CO)	ω(C-O)	References
top	-41.7 -34.7 -31					IRAS [64]; θ= 0 θ=0.33 θ=0.5
top					2090	TPD;IRAS; $\theta \to 0$ [65]
	-36					IRAS; $\theta \to 0$ [66]
	-35±1					TDS;LEED; θ=1/3 [67]
	-45.2/-37.8			505	2041	DFT;GGA: PW91/RPBE $\theta \to 1/4$ [5]
top	-48.9	1.85	1.17			Periodic DFT; RPBE+AER; θ=1/4 [87]
						DFT; cluster model [38];
top	-32.4	1.88	1.160		1975	(7/6)
hollow	-24.4	1.63	1.189		1702	(6/7)
	-44.4±0.4					Ref 16
	-34					UBI-QEP [18]
	-44±2 -37±1					IRAS [59] θ=0.05 θ=0.6

[a] see footnote to Table 1

Table 6. Physical characteristics of CO adsorption on Cu(111) [a]

site	E_{ads}	x_{0A}	h(C-O)	ω_A(M-CO)	ω(C-O)	References
top	-12					RAIRS, LEED; θ=1/3 [68]
top	-15.2					Periodic DFT; GGA; θ=1/4 [42]
top	-14.3	1.94 (fixed)	1.14 (fixed)		2162	Periodic DFT [69]; GGA
top brg fcc hollow fcc hollow	-16.8/-9.7 -17.1/-9.0 -19.4/-10.6 -19.1/-10.4	1.96/2.00 1.55/1.57 1.43/1.47 1.43/1.46	1.156/1.162 1.173/1.179 1.180/1.185 1.179/1.185	322/307 281/265 290/261 289/257	2046/2034 1901/1894 1854/1847 1859/1849	Periodic DFT [70]; θ=1/4 PW91/RPBE GGA
top	-11.3					TDS; low coverage [71]
top		1.91				ARPEFS [72]; θ=1/3
top					2075	RAIRS [73]; θ=1/3
top	-17.3/-9.7	1.96	1.156	323	2038	Periodic DFT [5]; θ=1/3 PW91/RPBE GGA
	-10.6					AES, LEED,EELS [74]; θ=1/3
	-11					LEED,TDS, UPS [75]; θ<1/3
	-12					UBI-QEP [18]
top				332	2077	EELS, RAIRS [76]; θ<1/3
top				345	2072	RAIRS [77]

[a] see footnote to Table 1

Table 7. Physical characteristics of CO adsorption on Ru(0001) [a]

site	E_{ads}	x_{0A}	h(C-O)	ω_A(M-CO)	ω(C-O)	References
top	-38.3±1.5 -41.9					TPD [78]; θ ~0 θ=0.33
top				445	1980	EELS; θ=0.2 [79]
top	-43.6/-39	2.03	1.166	439	1990	periodic DFT [5]; PW91/RPBE GGA
top	-41.5	1.90	1.17			Periodic DFT; RPBE+AER; θ=1/4 [87]
top hollow	-27.2 -21.7				1901 1648	DFT; cluster model [38]; (7/6) (6/7)
top		1.93±.04	1.1±.05			LEED [80]; θ=0.33
top				447	1990	HREELS [81]; θ=0.33
				436	1980	HREELS [82]; θ=0.1
top h-hollow f-hollow brg	-41.2 -39.2 -37.1 -36.4	1.92 2.18 2.18 2.11				Periodic DFT-GGA [84] θ=1/4

[a] see footnote to table 1

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II. Oxygen atomic adsorption on (111) metals

Table 8: Characteristics of oxygen atomic adsorption on Pd(111) surface

x_{0B}	ω_B	ΔE_{ads}	References and comments
		-53	TPD [1]; θ -->0
		-55	TPD [2]
	485		EELS [3-5]
1.24		-33.7	periodic DFT; θ =1/4 [6]
1.19	490	-43	periodic DFT; θ =1/4 [7]
		-42/-44	periodic DFT; GGA; PBE/rev PBE [8]
1.138	498	-42.3	DFT; cluster model; [9]

[a] Distance x_{0B}, in Angstrøm , frequency ω_B in cm $^{-1}$, energy ΔE_{ads} in kcal/mol, θ is the surface covering

Table 9: Characteristics of atomic adsorption of oxygen on Ni (111) surface [a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
1.16±0.08			NEXAFS [10]; θ=1/4 to 1/3
1.11±0.06			LEED [11];
		-105	calorimetry; low coverage [12]
1.08±0.02			NEXAFS [13]
1.21±0.09			LEED [14]
1.14		-97	Periodic DFT GGA; θ =1/3 [15]
			Periodic DFT; LSD [17]
1.16		-106	θ =1/4
1.12		-87.6	θ =1/2
		-122	Periodic DFT; GGA; PB91 θ =1/2 [16]
1.200	566	-88	DFT; cluster model [9]
		-112	CFSO-BEBO [58]

[a] See footnote to Table 8

Table 10: Characteristics of atomic adsorption of oxygen on Pt (111) surface[a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
	490		AES,EELS,UPS,TDS,LEED [18, 19]
		-47.8	high coverage limit
		-48 to -53	TDS, LEED , θ ~0 to ~ 1 [20]
	480		EELS, LEED, TDS [21, 22]
1.18 to 1.19			LEED [23, 24]
		-73±8 to -50	Calorimetry; θ =0 to 0.6 [25]
			AES, LEED, UPS, HREELS, DTP [27]
		-51	θ =0
	466	-43	θ =1/4
			NEXAFS [28]
			Scattering of molecular beams [29]
		-50.9	Low coverage
		-42	Near saturation
	475		HREELS, TDP; θ=0.2 to 0.45 [31]
1.23	470	-38	Periodic DFT; LSD; θ=0.5 [7, 32]
1.25		-28.1	Periodic DFT, GGA-BPW91 ; θ ~1 [33]
	510 to 530	-32.5	DFT; B3Lyp-GGA; 9/10/9 cluster; fixed Pt-Pt [34]
1.240	484		DFT; B3PW91; cluster model ; Pt_3 [35]
1.15	442	-49/-21	Periodic DFT; GGA-PW91/RPBE [36]
		-58 to -68	CFSO-BEBO [58]
1.262		-13	DFT, (6/3/1) cluster [64]
1.237		-27	DFT; B3LYP; cluster model; [9]
		-60	FDS [39] ; low coverage
		-49	75% of saturation
		-58 to -68	CFSO-BEBO [58]

[a] See footnote to Table 8;

Table 11: Characteristics of atomic adsorption of oxygen on Cu (111) surface [a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
	380		HREELS [40]
1.1 0.2±.2			SEXAFS [41]; fixed Cu-Cu relaxed Cu-Cu
	403		EELS [43]
		-86.2	Microcalorimetry[44]
1.35	550	-83.5	Five parameter Morse potential [46]
1.13	482	-68	Periodic DFT; GGA-PW91;θ =1/4 [47, 48]
1.23			DFT; cluster model ; two layers [49]

[a] see footnote to Table 8

Table 12 Characteristics of atomic adsorption of oxygen on Ir (111) surface [a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
	550		EELS [50]
	525		EELS ; θ =0.25 to 0.5 [51]
		-65±3	LEED, Auger ; θ ~0 [52]
1.22	483	-80.8	Periodic DFT; θ =¼ ; relax Ir-Ir [53]
1.244	630	-76.2	DFT; cluster model; [9]

[a] see footnote to Table 8

Table 13: Characteristics of atomic adsorption of oxygen on Ru(0001) surface [a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
		-96 to –86	LEED,AES [54]; θ from low to 0.5
	509	-99 to -86	DFT-GGA ; θ from 1/9 to 1 [56]
	500 to 600		SERS [67 b]
		-95 to -78	Periodic DFT-GGA ; θ from .25 to 1[68]
	516 to 596		EELS; θ from low to saturation [57]
1.278	612	-105	DFT; cluster model [9]

[a] see ref to Table 8; [b] gold coated by thin film of ruthenium

Table 14 : Characteristics of atomic adsorption of oxygen on Rh(111) surface[a]

x_{0B}	ω_B	ΔE_{ads}	References and comments
			periodic DFT-GGA [59]
1.24		-51.7	θ=0.25
1.23		-45	θ=0.5
1.16		-32.3	θ=1.0
1.22			LEED; θ=0.5 [60]
			LEED [61]
1.24±0.06			θ=0.25
1.25±0.05			θ=0.5
		-56±2	LEED, TPD, AES; θ ~0 [62]
		-56±2	TPD ,θ <0.15 [63]
1.212		-101	DFT; LDA-VWN ; (6/3/1) cluster [64]
			Periodic DFT; GGA -PW91/RPBE [66]
1.23		-95/-69	θ =0.25
1.191	572	-82.7	DFT, cluster model [9]

[a] see ref to Table 8

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III. Carbon dioxide adsorption on (111) metals

Table 15. Data compiled from published works and our data calculated in terms of cluster models characterizing of carbon dioxide adsorption on (111) transition metals [†]

Structure of cluster and references to published data	E_{ads}	*d / x*	*r / y*	A1 / A2 / A3	ω(C-O$_{(1)}$)/ω(C-O$_{(2)}$)/ ω(M-CO$_2$)
Ni(7/3): *b-b* [a]	-13.3	1.943/1.813	1.311/1.209	110/110/130	1148/1740/429
Ni(7/6/3): *b-b* [a]	-12.7	1.939/1.822	1.299/1.211	110/110/119	1088/1742/403
Ni(10/5): *b-b* [a]	-5.7	1.964/1.878	1.280/1.210	107/107/134	1110/1761/360
Ni(7/6/3): *b-h* [a]	-18.8	1.885/1.740	1.358/1.203	113/105/128	934/1754/421
Ref 2 [b]	-6.5				
Ref 3 [d]	7		1.224/1.203		
Cu(7/6/3): *b-h*					
Ref 2 [b]	-5.3				
Ref 4 [e]	-4 to -5				
Rh(7/3) : *b-b* [a]	-5.3	2.104/1.959	1.300/1.210	111/111/130	1052/1742/339
Rh(7/6/3): *b-b* [a]	-4.3	2.071/1.946	1.307/1.209	110/110/121	1061/1741/368
Rh(7/6/3): *b-h* [a]	-15.7	2.035/1.859	1.371/1.201	114/107/128	880/1761/390
Ref 2 [b]	-5.2				
Refs 5, 6 [e]	-6 to -7				
Ir(7/3): *b-b* [a]	9.2	2.122/1.983	1.336/1.203	111/111/126	950/1756/350
Ir(7/6/3): *b-b* [a]	-3.1	2.106/1.991	1.336/1.205	110/110/121	990/1753/388
Ir(7/6/3): *b-h* [a]	-14.3	2.051/1.902	1.432/1.194	112/105/134	656/1809/348
Ref 2 [b]	-4.3				
Pd(7/3): *b-b* [a]	3.3	2.181/2.066	1.232/1.199	109/109/144	1180/1031/non-identif.
Pd(7/6/3): *b-b* [a]	0.9	2.114/1.986	1.263/1.192	110/110/113	1140/1843/278
Pd(7/6/3): *b-h* [a]	-1.9	2.051/1.866	1.307/1.197	114/108/120	1026/1808/320
Ref 7 [c]	-1.8				
Ref 2 [b]	-3.8				
Refs 8, 9 [e]	-6 to -7				
Ref 10 [f]	5	2.049	1.279/1.211	114/114/133	1140/1782/?

Pt(7/3):	*b-b* [a]	10.3	2.197/2.055	1.277/1.197	112/112/135	1085/1832/197
Pt(7/6/3):	*b-h* [a]	15.8	2.052/1.872	1.364/1.193	114/108/126	894/1811/ non-identif.
Ref 2 [b]		-3.6				
Refs 11, 12 [e]		-2.5 to -7				

† DFT method as implemented in Gaussian 03 [1] was employed. Calculations were performed in terms of cluster models with the use of B3LYP functional; the basis set used for metal atoms is a LANL set for the effective core potentials of double-ζ type (LANL2DZ). For oxygen and carbon, the cc-pVDZ basis set was used. *b-b* and *b-h* denote *bond-bond* (Figs. 1a, b, and c) and *bond-hollow* (Fig. 1d) complexes, respectively. Denotations of the geometric characteristics are shown in Fig.2; (m/n/k) denotes three-layer cluster, (m/n) denotes two-layer cluster; E_{ads} in kcal/mol, d, y_1 and y_2 in Å, angles A1, A2 and A3 in degrees, and frequencies ω in cm^{-1}; [a] our cluster calculation; [b] semi-empirical estimation using approach of Ref 13; [c] periodic DFT calculations for *b-h* configuration; [d] periodic DFT calculations for *b-b* configuration; [e] experimental estimation; [f] DFT calculation using two-layer cluster Pd(10/5) for *b-b* configuration; basis set for CO_2 is 6-311^{++}g(2d).

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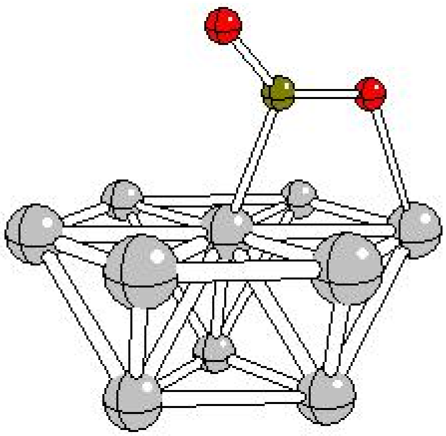
Figures 1a-d. Cluster models used for calculations of the CO_2 chemisorption on (111) metals



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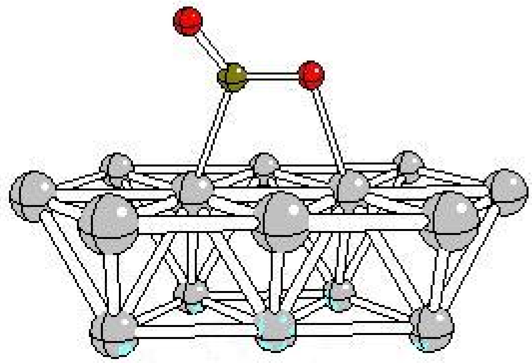

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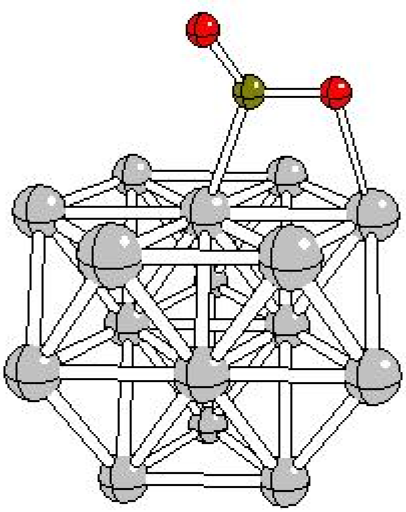

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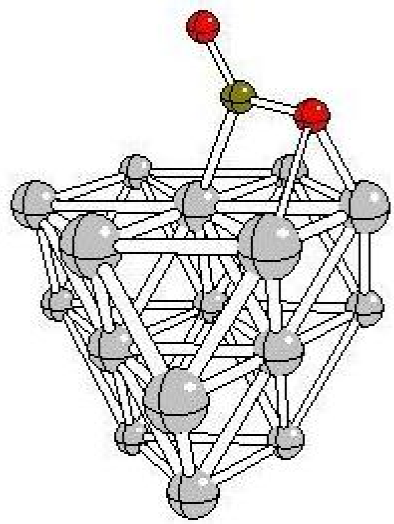

d

Figure 2. Structure characteristics of a chemisorbed CO_2 molecule