Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for *Gas-Phase and Solid-State Electronic Structure Analysis and DFT Benchmarking of HfCO*

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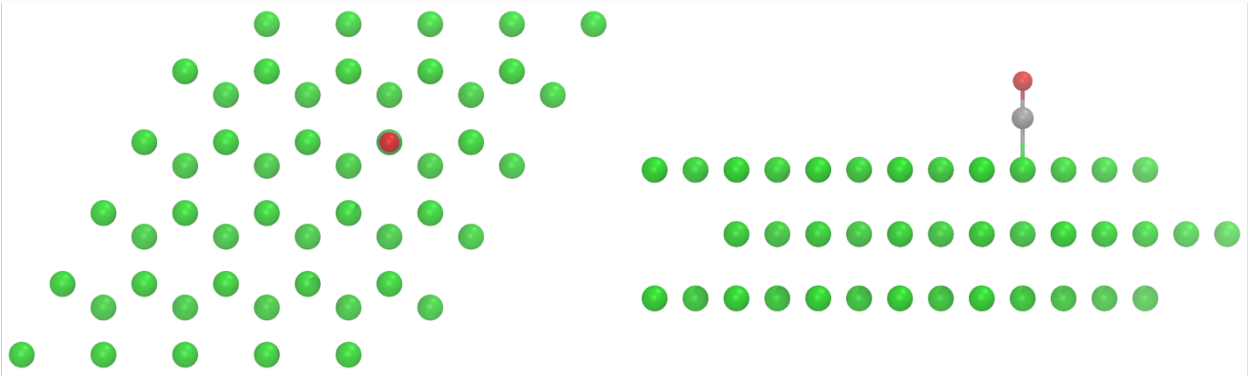

Figure S1. Geometry of CO molecule on periodic (001) surface of hexagonal Hf optimized with the BLYP functional. The C atom is 2.22 Å from the Hf surface and C-O bond length is 1.17 Å.

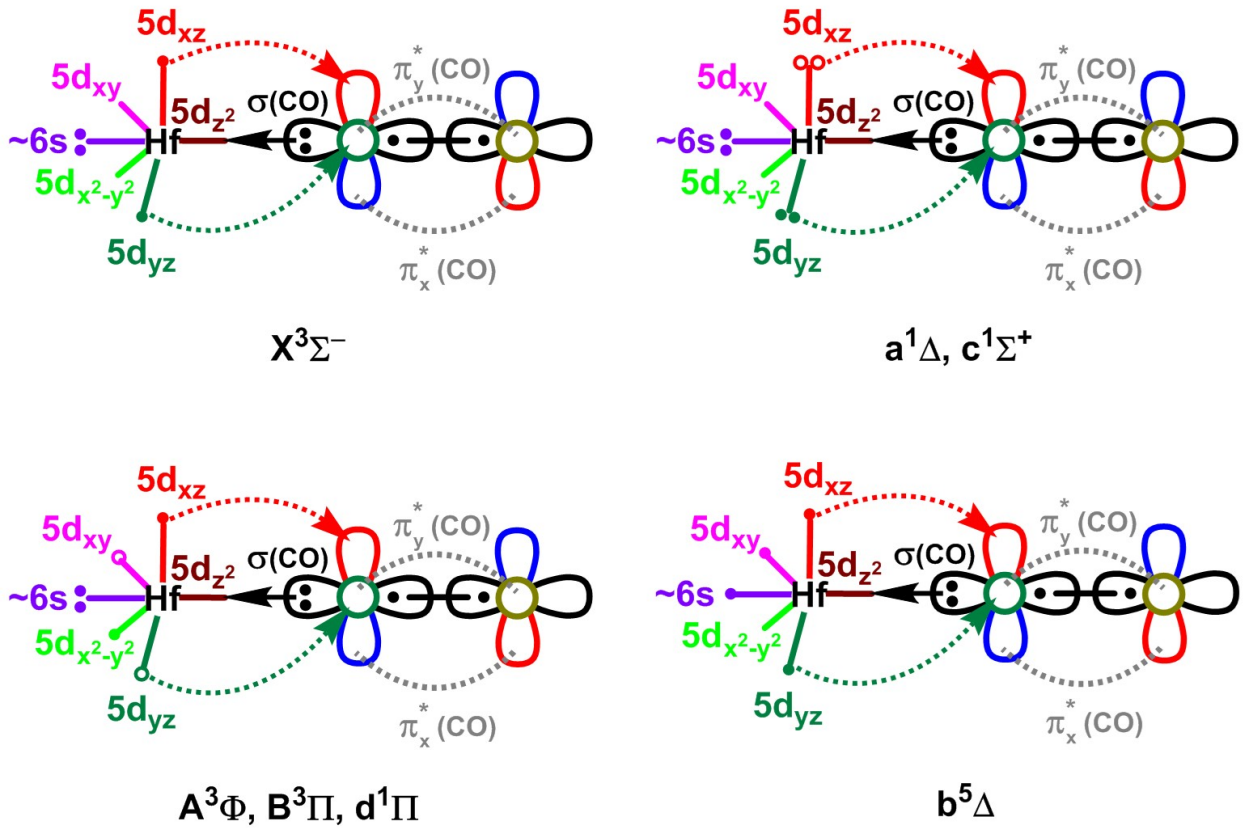

Figure S2. Proposed valence-bond-Lewis (vbL) diagrams for the seven lowest electronic states of HfCO. The π_x and π_y bonds of CO are omitted for clarity. The two $5d_{xz}$ and $5d_{yz}$ electrons of $X^3\Sigma^-$ have the same spin. The multireference $(1\pi_x)^2 \pm (1\pi_y)^2$ components of the $a^1\Delta$ and $c^1\Sigma^+$ states are shown by electron pairs with open and solid circles. Similarly, the π^1d^1 electron combinations of $A^3\Phi$, $B^3\Pi$, and $d^1\Pi$ are depicted in open and solid circles. See main text Table 1 for more details on electronic configurations.

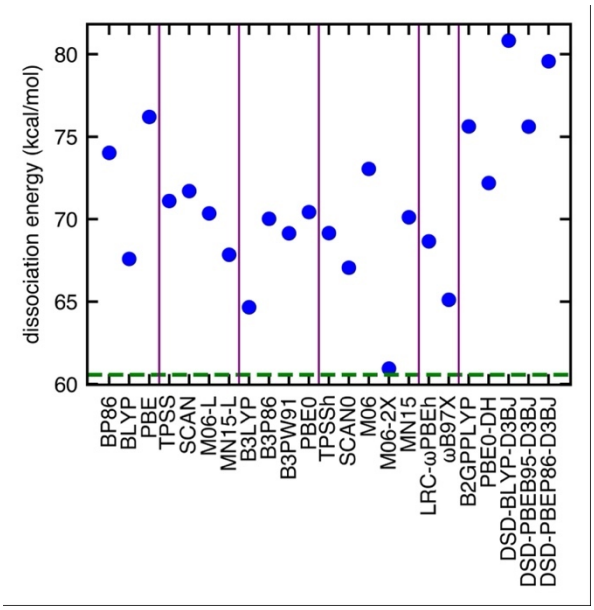

Figure S3. Dissociation energy (D_e, in kcal/mol) of HfCS calculated with different DFT functionals using the def2-QZVP basis set (blue dots). Each class of density functionals is separated with vertical purple lines and ordered by the rung on Jacob's ladder (left to right: GGA, meta-GGA, global GGA hybrid, meta-GGA hybrid, range-separated hybrid, and double hybrid). The horizontal green dashed line represents the CCSD(T)/TZ dissociation energy of HfCS.

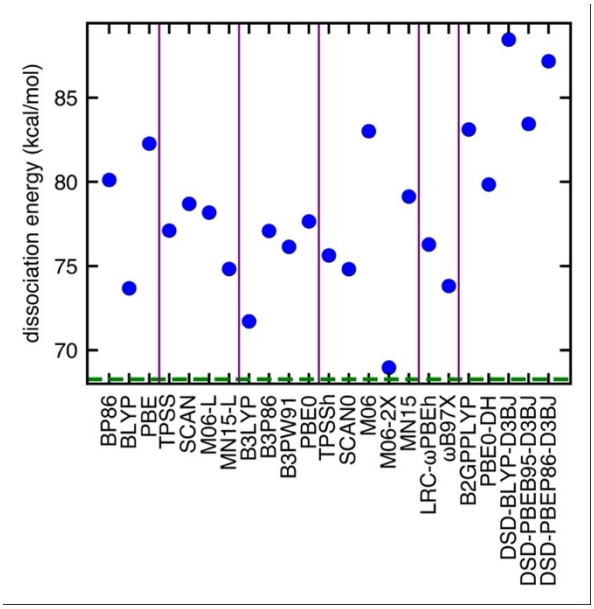

Figure S4. Dissociation energy (D_e, in kcal/mol) of HfCSe calculated with different DFT functionals using the def2-QZVP basis set (blue dots). Each class of density functionals is separated with vertical purple lines and ordered by the rung on Jacob's ladder (left to right: GGA, meta-GGA, global GGA hybrid, meta-GGA hybrid, range-separated hybrid, and double hybrid). The horizontal green dashed line represents the CCSD(T)/TZ dissociation energy of HfCSe.

Table S1. Dissociation energy (D_e) of HfCO (kcal/mol) calculated with different DFT functionals using the def2-QZVP basis set and % DFT D_e error with respect to the CCSD(T)-A5Z D_e (29.96 kcal/mol).

	DFT functional	D_e	% DFT error
GGA	BP86	41.37	38.07
	BLYP	35.02	16.87
	PBE	43.19	44.17
meta-GGA	TPSS	38.59	28.81
	SCAN	38.60	28.84
	M06-L	37.07	23.74
	MN15-L	36.95	23.34
hybrid	B3LYP	31.07	3.72
	B3P86	36.35	21.33
	B3PW91	35.46	18.37
	PBE0	36.35	21.34
meta-GGA hybrid	TPSSh	36.11	20.54
	SCAN0	32.83	9.57
	M06	38.38	28.11
	M06-2X	27.62	-7.81
	MN15	38.56	28.72
range-separated hybrid	LRC-ωPBEh	35.24	17.62
	ωB97X	30.24	0.95
double hybrid	B2GP-PLYP	40.61	35.53
	PBE0-DH	37.39	24.81
	DSD-BLYP-D3BJ	45.32	51.27
	DSD-PBEB95-D3BJ	40.63	35.61
	DSD-PBEP86-D3BJ	44.69	49.18

Table S2. Dissociation energy (D_e) of HfCS (kcal/mol) calculated with different DFT functionals using the def2-QZVP basis set and % DFT D_e error with respect to the CCSD(T)-TZ D_e (60.58 kcal/mol).

	DFT functional	D_e	% DFT error
GGA	BP86	74.02	22.19
	BLYP	67.60	11.59
	PBE	76.20	25.79
meta-GGA	TPSS	71.11	17.38
	SCAN	71.71	18.38
	M06-L	70.35	16.13
	MN15-L	67.85	12.01
hybrid	B3LYP	64.66	6.74
	B3P86	70.03	15.60
	B3PW91	69.14	14.14
	PBE0	70.43	16.26
meta-GGA hybrid	TPSSh	69.16	14.16
	SCAN0	67.06	10.70
	M06	73.05	20.59
	M06-2X	60.95	0.61
	MN15	70.13	15.76
range-separated hybrid	LRC-ωPBEh	68.66	13.34
	ωB97X	65.12	7.49
double hybrid	B2GP-PLYP	75.63	24.84
	PBE0-DH	72.20	19.18
	DSD-BLYP-D3BJ	80.83	33.43
	DSD-PBEB95-D3BJ	75.61	24.82
	DSD-PBEP86-D3BJ	79.57	31.35

Table S3. Dissociation energy (D_e) of HfCSe (kcal/mol) calculated with different DFT functionals using the def2-QZVP basis set and % DFT D_e error with respect to the CCSD(T)-TZ D_e (68.28 kcal/mol).

	DFT functional	D_e	% DFT error
GGA	BP86	80.12	17.34
	BLYP	73.68	7.91
	PBE	82.28	20.50
meta-GGA	TPSS	77.11	12.94
	SCAN	78.70	15.26
	M06-L	78.17	14.49
	MN15-L	74.83	9.60
hybrid	B3LYP	71.72	5.04
	B3P86	77.09	12.90
	B3PW91	76.15	11.53
	PBE0	77.66	13.74
meta-GGA hybrid	TPSSh	75.64	10.78
	SCAN0	74.82	9.57
	M06	83.01	21.57
	M06-2X	68.97	1.02
	MN15	79.13	15.89
range-separated hybrid	LRC-ωPBEh	76.28	11.72
	ωB97X	73.82	8.12
double hybrid	B2GP-PLYP	83.12	21.73
	PBE0-DH	79.84	16.93
	DSD-BLYP-D3BJ	88.46	29.55
	DSD-PBEB95-D3BJ	83.45	22.22
	DSD-PBEP86-D3BJ	87.17	27.67

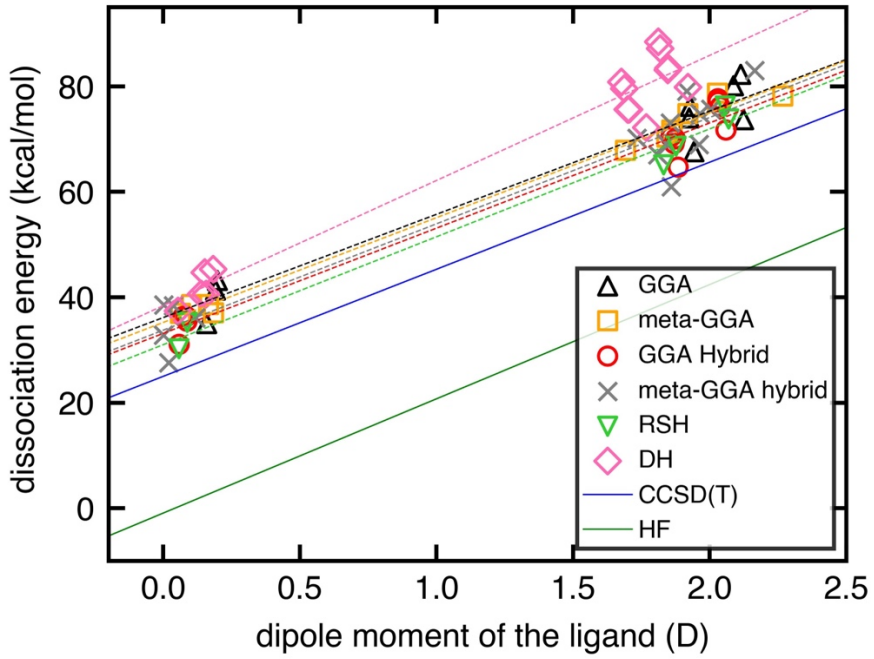

Figure S5. Dissociation energy (D_e, in kcal/mol) of HfCX vs. dipole moment (μ, in D) of the CX for X = O, S, Se computed with different DFT functionals using the def2-QZVP basis set (trendlines of different functionals are depicted in dashed lines). The trendlines of HF/cc-pVTZ(-PP) and CCSD(T)/cc-pVTZ(-PP) are shown in green and blue solid lines with the y = 21.66x - 0.92 (R^2 = 0.97) and y = 20.30x + 25.01 (R^2 = 0.99) fittings, respectively. Trendlines of GGA, meta-GGA, GGA Hybrid, meta-GGA hybrid, RSH, and DH are y = 19.58x + 36.16 (R^2 = 0.95), y = 19.86x + 35.23 (R^2 = 0.99), y = 19.96x + 33.16 (R^2 = 0.98), y = 20.17x + 33.77 (R^2 = 0.94), y = 20.46x + 31.02 (R^2 = 0.98), and y = 23.73x + 38.42 (R^2 = 0.96), respectively.

Table S4. Triplet-Quintet energy gap ($\Delta E_{T\text{-}Q}$) of HfCO (kcal/mol) calculated with different DFT functionals using the def2-QZVP basis set and % DFT $\Delta E_{T\text{-}Q}$ error with respect to CCSD(T)-TZ $\Delta E_{T\text{-}Q}$ (22.36 kcal/mol).

	DFT functional	$\Delta E_{T\text{-}Q}$	% DFT error
GGA	BP86	12.74	-43.02
	BLYP	17.70	-20.85
	PBE	11.41	-48.95
meta-GGA	TPSS	9.35	-58.19
	SCAN	4.46	-80.06
	M06-L	22.49	0.60
	MN15-L	19.32	-13.59
hybrid	B3LYP	16.91	-24.37
	B3P86	12.85	-42.55
	B3PW91	9.61	-57.03
	PBE0	10.32	-53.83
meta-GGA hybrid	TPSSh	9.43	-57.83
	SCAN0	5.81	-74.03
	M06	36.53	63.40
	M06-2X	21.47	-3.96
	MN15	28.24	26.28
range-separated hybrid	LRC-ωPBEh	10.29	-53.98
	ωB97X	31.81	42.27
double hybrid	B2GP-PLYP	20.10	-10.11
	PBE0-DH	11.72	-47.56
	DSD-BLYP-D3BJ	21.07	-5.76
	DSD-PBEB95-D3BJ	21.97	-1.73
	DSD-PBEP86-D3BJ	20.71	-7.36

Table S5. Adiabatic ionization energy (IE) of HfCO (eV) calculated with different DFT functionals using the def2-QZVP basis set and % DFT IE error with respect to CCSD(T)-TZ IE (6.974 eV).

	DFT functional	IE	% DFT error
GGA	BP86	7.146	2.47
	BLYP	7.056	1.18
	PBE	7.003	0.42
meta-GGA	TPSS	6.871	-1.48
	SCAN	6.813	-2.31
	M06-L	7.141	2.39
	MN15-L	7.219	3.51
hybrid	B3LYP	7.095	1.74
	B3P86	7.169	2.79
	B3PW91	6.879	-1.36
	PBE0	6.853	-1.74
meta-GGA hybrid	TPSSh	6.832	-2.04
	SCAN0	6.760	-3.06
	M06	7.547	8.22
	M06-2X	7.176	2.89
	MN15	7.354	5.45
range-separated hybrid	LRC-ωPBEh	6.780	-2.78
	ωB97X	7.333	5.14
double hybrid	B2GP-PLYP	7.011	0.54
	PBE0-DH	6.837	-1.97
	DSD-BLYP-D3BJ	7.023	0.70
	DSD-PBEB95-D3BJ	6.941	-0.48
	DSD-PBEP86-D3BJ	7.025	0.74