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J879-1

Supplementary material:

Table 1. Harmonic vibrational frequencies and IR intensities for the ground state of VH_4 at the TZP CISD level of theory.

VH_4					VD_4		
Symmetry	Mode	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)
a_1	V–H stretch	1961	1863	0.0	1387	1318	0
b_2	V—H stretch	1911	1816	541	1375	1306	287
e	V—H stretch	1872	1878	502	1342	1275	270
b_1	H—V—H deformation	679	645	0	480	456	0
a_1	H—V—H deformation	554	526	0	392	372	0
e	H—V—H deformation	458	435	169	331	315	88
b_2	H—V—H deformation	253	240	54	181	172	27

[a] The vibrational frequencies were scaled by a factor 0.95 to account for anharmonicity and higher level correlation effects.

J879-2

Supplementary material:

Table 2. Total energies for the TiH_2 molecule at the TZP CISD level of theory.[a]

Electronic state	Electronic configuration	Total energy (hartree)	
		CISD	CCSD[b]
$^3B_1$	$6a_1^2\ 3b_2^2\ 7a_1\ 3b_1$	-849.79074 (-849.84834) **-849.84965**	-849.81282 (-849.876395) **-849.87785**
$^3A_1$	$6a_1^2\ 3b_2^2\ 7a_1\ 8a_1$	-849.79068 (-849.84823)	-849.81269 (-849.87619)
$^3\Delta_g$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g\ 5\sigma_g$	-849.78972	-849.810736
$^3A_2$	$6a_1^2\ 3b_2^2\ 7a_1\ 1a_2$	-849.78180	-849.80159
	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g\ \pi_g$	-849.78122	-849.80045
	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2$	-849.73567	-849.76094

a. The values in parentheses are at the TZP+f CISD level of theory; and the values in boldface are at the TZP(f,d) CISD level of theory. Spherical d and f functions are used.

b. The CCSD energies are single point energies at the CISD optimized geometries. THe CCSD(T) single point energy for $^3B_1$ ground state is -894.88611 au.

J879-3

Supplementary material:

Table 3. Total energies for the VH_2 molecule at the TZP CISD level of theory.[a]

Electronic state	Electronic configuration	Total energy (hartree)	
		CISD	CCSD [b]
$^4B_2$	$6a_1^2\ 3b_2^2\ 7a_1$ $3b_1\ 1a_2$	-944.26109 (-944.33453) **-944.33828**	-944.28291 (-944.36415) **-944.36837**
$^4B_1$	$6a_1^2\ 3b_2^2\ 7a_1$ $8a_1\ 3b_1$	-944.25791 **-944.33382**	-944.28186 **-944.36598**
$^4A_2$	$6a_1^2\ 3b_2^2\ 7a_1$ $3b_1 4b_2$	-944.25791	-944.28186
$^4\Pi_g$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2\ 1\pi_g$	-944.25991 **-944.33623**	-944.28007 **-944.36384**
$^4\Sigma_g^-$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2\ 5\sigma_g$	-944.25663	-944.27908
$^4A_2$	$6a_1^2\ 3b_2^2\ 7a_1\ 8a_1 1a_2$	-944.25170	-944.27742
$^4\Delta_g$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g\ 1\pi_g^2$	-944.25767	-944.27645
$^2A_1$	$6a_1^2\ 3b_2^2\ 3b_1^2\ 7a_1$	-944.19253	-944.21932
$^2\Gamma_g^-$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2\ 5\sigma_g$	-944.19098	-944.21615
$^2A_2$	$6a_1^2\ 3b_2^2\ 3b_1^2\ 1a_2$	-944.18587	-944.21269
	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2 1\pi_g$	-944.18495	-944.21071
$^2B_1$	$6a_1^2\ 3b_2^2\ 3b_1^2\ 4b_1$	-944.04820	

a. The values in parentheses are at the TZP+f CISD level of theory; and the values in boldface are at the TZP(f,d) CISD level of theory.

b. The CCSD energies are single point energies at the CISD optimized geometries. The CCSD(T) single point energy for $^4B_2$ ground state is -944.37669 au and that for $^2A_1$ state is -944.31545 au.

J879-4

Supplementary material:

Table 4. Total energies for the CrH_2 molecule at the TZP CISD level of theory.[a]

Electronic state	Electronic configuration	Total energy (hartree)[b]	
		CISD	CCSD
$^5B_2$	$6a_1^2\ 3b_2^2\ 7a_1\ 3b_1\ 1a_2\ 8a_1$	-1044.68803 **-1044.77999**	-1044.71538 -1044.81764[c]
$^5\Sigma_g^+$	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2\ 1\pi_g^2$	-1044.69406	-1044.71319
	$4\sigma_g^2\ 3\sigma_u^2\ 1\delta_g^2\ 1\pi_g\ 5\sigma_g$	-1044.59861	-1044.62199 -1044.72316[c]
$^3A_2$	$6a_1^2\ 3b_2^2\ 3b_1^2\ 7a_1\ 1a_2$	-1044.59527	-1044.61908

a. The values in boldface are at the TZP(f,d) CISD level of theory.

b. The CCSD energies are single point energies at the CISD optimized geometries.

c. This is the TZP(f,d) CCSD total energy at the TZP(f,d) CISD equilibrium geometry. The CCSD(T) single point energies are -1044.82781 au for $^5B_2$ ground state and -1044.73343 au for the lowest triplet state.

J879-5

Supplementary material:

Table 5. Harmonic vibrational frequencies and IR intensities for $^2A''$ $VH_2 \cdot H_2$ at the TZP CISD level of theory.

		$VH_2 \cdot H_2$			$VD_2 \cdot D_2$		
No.	Mode	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)
1	H–H stretch	2776	2637	22	1967	2793	10
2	H—V—H symm stretch	1746	1658	81	1244	1060	39
3	H—V—H asymm stretch	1696	1611	49	1219	1102	23
4	V···H–H bend	1655	1572	367	1172	705	182
5	V···H_2 stretch	828	786	217	589	380	118
6	H—V···H bend	636	604	166	451	310	81
7	V···H–H bend	471	447	269	339	302	137
8	H—V···H bend	307	291	807	221	181	342
9	H—V···H bend	300	285	231	216	158	192

[a] The vibrational frequencies were scaled by a factor of 0.95 to account for anharmonicity and higher level correlation effects.

J879-6

Supplementary material:

Table 6. Harmonic vibrational frequencies and IR intensities for ^3B $CrH_2 \cdot H_2$ at the TZP CISD level of theory.

		$CrH_2 \cdot H_2$			$CrD_2 \cdot D_2$		
No	Mode	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)	ω (cm^{-1})	ω (cm^{-1}) scaled[a]	IR Intensity (km/mol)
1	H–H stretch	3884	3689	85	2747	2609	43
2	H—Cr—H symm stretch	1749	1661	39	1238	1176	19
3	H—Cr—H asymm stretch	1609	1528	938	1160	1102	481
4	Cr···H–H bend	1399	1329	6	990	855	4
5	Cr···H_2 stretch	701	666	101	502	476	39
6	H—Cr····H bend	541	514	219	390	370	123
7	Cr···H–H bend	425	404	276	306	290	160
8	H—Cr···H bend	418	397	29	296	281	10
9	H—Cr····H bend	397	377	121	284	269	50

[a] The vibrational frequencies were scaled by a factor of 0.95 to account for anharmonicity and higher level correlation effects.

Supplementary material:

J879-7

Table 7. Structures and energies for the $MH_2 \cdot H_2$ (C_{2v}, side-on) at the TZP CISD level of theory.[a]

	Electronic configuration	conformation	Total energy	H–H	M-H	H_2..M	H-M-H
				r (Å)	r (Å)	r (Å)	θ
$TiH_2 \cdot H_2$	$7a_1^2\ 3b_2^2\ 8a_1\ 9a_1$	planar	-850.95064	0.745	1.828	3.543	179.0°
	$7a_1^2\ 3b_2^2\ 8a_1\ 9a_1$	perpendicular	-850.94994	0.745	1.838	3.254	164.3°
	$7a_1^2\ 3b_2^2\ 8a_1\ 3b_1$	planar	-850.95081	0.746	1.827	3.412	179.0°
	$7a_1^2\ 3b_2^2\ 8a_1\ 3b_1$	perpendicular	-850.95140	0.746	1.808	3.547	149.0°
	$7a_1^2\ 3b_2^2\ 8a_1 1a_2$	planar	-850.94332	0.743	1.853	3.536	152.0°
	$7a_1^2\ 3b_2^2\ 8a_1 1a_2$	perpendicular	-850.94298	0.748	1.845	3.759	150.7°
$VH_2 \cdot H_2$	$7a_1^2 3b_2^2 8a_1 3b_1 4b_2$	planar	-945.42999 **-945.45827**	0.762	1.786	2.067	173.9°
	$7a_1^2 3b_2^2 8a_1 3b_1 4b_2$	perpendicular	-945.42629 **-945.45429**	0.753	1.788	2.154	170.9°
	$7a_1^2 3b_2^2 8a_1 3b_1 1a_2$	planar	-945.42239	0.746	1.786	3.567	145.6°
	$7a_1^2 3b_2^2 8a_1 3b_1 1a_2$	perpendicular	-945.42215	0.745	1.690	3.726	144.8°
	$7a_1^2 3b_2^2 8a_1 3b_1 9a_1$	planar	-945.41904	0.746	1.769	3.522	145.0°
	$7a_1^2 3b_2^2 8a_1 3b_1 9a_1$	perpendicular	-945.41888	0.746	1.768	3.618	144.4°
	$7a_1^2 3b_2^2 3b_1^2 1a_2$	planar	-945.35459 **-945.38882**	0.753	1.770	2.181	150.3°
	$7a_1^2 3b_2^2 3b_1^2 1a_2$	perpendicular	-945.37270 **-945.41739**	0.919	1.702	1.710	122.0°
	$7a_1^2 3b_2^2 3b_1^2 8a_1$	perpendicular	-945.36266 **-945.40729**	0.842	1.714	1.786	117.0°
$CrH_2 \cdot H_2$	$7a_1^2 3b_2^2 8a_1 3b_1 9a_1$ $1b_2$	planar	-1045.85915 **-1045.8841**	0.741	1.686	3.087	125.0°
	$7a_1^2 3b_2^2 8a_1 3b_1 9a_1$ $1b_2$	perpendicular	-1045.85076 **-1045.8841**	0.746	1.684	3.120	124.7
	$7a_1^2 3b_2^2 8a_1 3b_1 4b_2$ $1a_2$	perpendicular	-1045.85914	0.746	1.731	2.219	173.7°
	$7a_1^2 3b_2^2 3b_1^2 4b_1 4b_2$	perpendicular	-1045.77384 **-1045.8089**	0.771	1.714	1.832	125.0°
	$7a_1^2 3b_2^2 3b_1^2 8a_1 4b_1$	perpendicular	-1045.75856 **-1045.7996**	0.763	1.662	2.047	110.0°

a. The values in boldface are the CCSD energies at the CISD optimized geometries.