Electronic Supplementary Information

Ab Initio Electronic Structure Analysis of Ground and Excited States of HfN$^{0,+}$

Isuru R. Ariyarathna

Physics and Chemistry of Materials (T-1), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Email: isuru@lanl.gov

Contents

Table S1. The dominant molecular orbital compositions of HfN obtained at the state average CASSCF level.

Molecular orbital[a]	Composition
1σ	87.4% 2s (N)
2σ	63.8% $2p_z$ (N) + 18.2% $5d_{z^2}$ (Hf) + 17.3% 6s (Hf)
3σ	72.4% 6s (Hf) + 15.2% $5d_{z^2}$ (Hf)
$1\pi_y$	57.4% $2p_y$ (N) + 19.0% $5d_{yz}$ (Hf)
$2\pi_y$	18.0% $6p_y$ Hf + 47.3% $5d_{yz}$ Hf + 9.7% $2p_y$ (N)
$1\delta_{x^2-y^2}$	100% $5d_{x^2-y^2}$ (Hf)

[a] Contours of molecular orbitals are given in Figure 2 of the paper.

Table S2. Bond length (r_e, Å), excitation energy (T_e, cm^{-1}), harmonic vibrational frequency (ω_e, cm^{-1}), and anharmonicity ($\omega_e x_e$, cm^{-1}) of the low-lying Ω = 1/2, 1/2, 3/2, 1/2, 3/2, and 5/2 spin-orbit states of HfN at MRCI [cc-pVQZ-PP (60ECP) of Hf and aug-cc-pVQZ of N].

Ω	r_e	T_e	ω_e	$\omega_e x_e$	Composition
1/2	1.736	0	916	4.9	99.652% X$^2\Sigma^+$, 0.346% 1$^2\Pi$
1/2	1.781	6264	862	18.4	94.913% 2$^2\Sigma^+$, 5.026% 1$^2\Pi$, 0.061% X$^2\Sigma^+$
3/2	1.866	7216	939	12.6	100% 1$^2\Pi$
1/2	1.847	8015	1095	7.9	79.096% 1$^2\Pi$, 20.006% 2$^2\Sigma^+$,
3/2	1.825	13498	795	1.9	100% 1$^2\Delta$
5/2	1.825	15796	797	2.0	100% 1$^2\Delta$

Table S3. Dissociation energy with respect to ground state fragments (D_e, kcal/mol), bond length (r_e, Å), harmonic vibrational frequency (ω_e, cm^{-1}), and anharmonicity ($\omega_e x_e$, cm^{-1}) of HfN(X$^2\Sigma^+$) and HfN$^+$(X$^1\Sigma^+$) at the CCSD(T) with cc-pwCVTZ-PP (60ECP) of Hf and aug-cc-pVTZ of N basis set [TZ-C-CCSD(T)]. The 5s^{2}5p^6 core electrons of Hf are correlated.

Species	D_e	r_e	ω_e	$\omega_e x_e$
HfN(X$^2\Sigma^+$)	128.55	1.724	939	3.8
HfN$^+$(X$^1\Sigma^+$)	111.28	1.679	990	6.7

Table S4. Bond length (r_e, Å), excitation energy (T_e, cm^{-1}), harmonic vibrational frequency (ω_e, cm^{-1}), and anharmonicity ($\omega_e x_e$, cm^{-1}) of the low-lying Ω spin-orbit states of HfN$^+$ at MRCI [cc-pVQZ-PP (60ECP) of Hf and aug-cc-pVQZ of N].

Ω	r_e	T_e	ω_e	$\omega_e x_e$	Composition
0$^+$	1.698	0	955	6.5	99.65% X$^1\Sigma^+$, 0.34 % $^3\Pi$
0$^-$	1.766	7939	920	7.0	97.71% $^3\Sigma^+$, 2.30% $^3\Pi$
1	1.765	7950	922	6.8	98.19% $^3\Sigma^+$, 1.14% $^3\Pi$, 0.68% $^1\Pi$
0$^+$	1.774	8517	928	11.7	96.70% 2$^1\Sigma^+$, 3.26 $^3\Pi$
2	1.843	10605	839	5.0	100% $^3\Pi$
1	1.845	10749	866	4.1	89.75% $^3\Pi$, 2.39% $^3\Sigma^+$, 7.86 $^1\Pi$
0$^-$	1.843	11094	904	1.1	92.32% $^3\Pi$, 7.67% $^3\Sigma^+$
0$^+$	1.842	11215	911	4.4	89.76% $^3\Pi$, 1.50% X$^1\Sigma^+$, 8.75% 2$^1\Sigma^+$
1	1.850	12171	890	1.2	90.45% $^1\Pi$, 6.37% $^3\Pi$, 3.18% $^3\Sigma^+$
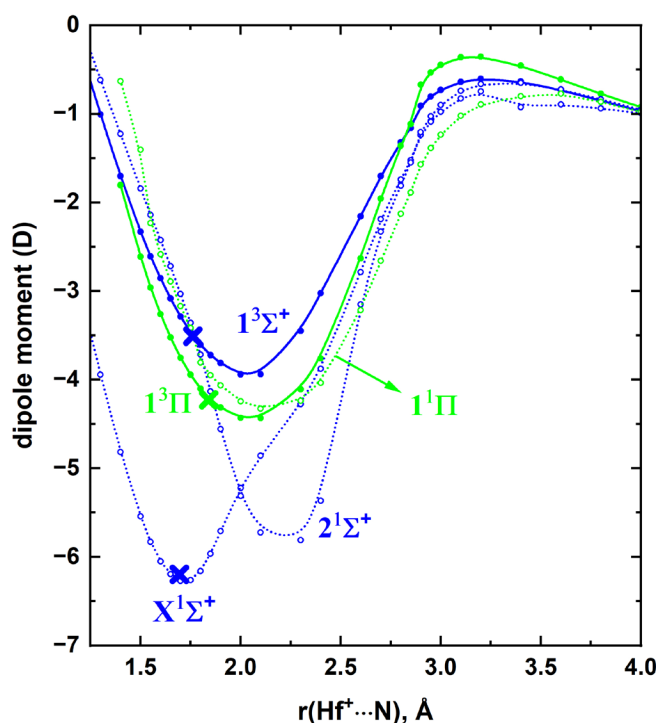
Figure S1. MRCI DMCs of the lowest five electronic states of HfN$^+$ as a function of Hf$^+\cdots$N distance [r(Hf$^+\cdots$N), Å]. The CCSD(T) μ values of X$^1\Sigma^+$, $^3\Pi$, and $^3\Sigma^+$ states calculated at the equilibrium bond distances are depicted in blue (at -6.20 D), green (at -4.23 D), and blue (at -3.51 D) cross marks, respectively.