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Ab initio electronic structures and total internal partition sums of $\text{FeH}^{+}/2^{+}$

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In the present work, we studied 27 FeH^+ and 6 FeH^{2+} electronic states using multireference configuration interaction (MRCI), Davidson-corrected MRCI (MRCI+Q), and coupled cluster singles doubles and perturbative triples [CCSD(T)] wavefunction theory (WFT) calculations conjoined with large quadruple- ζ and quintuple- ζ quality correlation consistent basis sets. We report their potential energy curves (PEC), energy related properties, spectroscopic parameters, and spin-orbit couplings. Dipole moment curves (DMC) and transition dipole moment curves (TDMC) of several low-lying electronic states of FeH^+ and FeH^{2+} are also introduced. The ground state of FeH^+ is a single-reference $X^5\Delta$ ($6\sigma^27\sigma^13\pi^21\delta^3$) with an adiabatic D_0 of ~ 52 kcal mol $^{-1}$, which is in agreement with the experimental value. The states with the largest adiabatic binding energies of FeH^{2+} ($^4\Pi$ and $^4\Delta$) are multireference in nature with an approximate D_0 of 22 kcal mol $^{-1}$. We used CCSD(T) μ of the $\text{FeH}^+(X^5\Delta)$ to assess the density functional theory (DFT) errors associated with a series of functionals that span multiple rungs of Jacob's ladder of density functional approximation (DFA) and observed a general trend of improving μ when moving to more expensive functionals at the higher rungs. We expect weak spectral bands to be produced from the low-lying electronic states of FeH^{2+} and FeH^+ due to their lower transition μ values. Lastly, we present results for the total internal partition function sums (TIPS) of FeH^+ and FeH^{2+} , which have not been presented in the literature before.

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1. Introduction

The diatomic iron hydride cation FeH^+ is predicted to be abundant in cool stellar atmospheres.¹ However, due to the deficiency of available laboratory spectroscopic data on FeH^+ , its astronomical presence is yet to be observed. Aiming to guide and motivate experimental analysis of FeH^+ so far, a series of theoretical and computational attempts have been made specifically for gaining insight into its spectral features.

The first observation of the FeH^+ goes back to the 1979 Mysov *et al.*'s mass spectroscopic fragment analysis study of $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Fe}$.² Five years later, Halle, Klein, and Beauchamp analyzed the thresholds of the $\text{Fe}^+ + \text{H}_2$ and $\text{Fe}^+ + \text{D}_2$ reactions using ion beam apparatus and obtained the D_0 of FeH^+ (59 ± 5 kcal mol $^{-1}$).³ In 1986, Schilling *et al.*⁴ performed an *ab initio*

generalized valence bond plus configuration interaction study and assigned a $^5\Delta$ ground state with a 47.0 kcal mol $^{-1}$ D_0 to FeH^+ which is significantly lower than the experimental value obtained by Halle *et al.*³ In the same year, Elkind and Armentrout carried out a guided ion beam mass spectrometric study and reported a D_0 of 48.9 ± 1.4 kcal mol $^{-1}$ for FeH^{+5} which is in agreement with Schilling *et al.*'s work.⁴ Furthermore, they intuitively projected low-lying $^5\Pi$ and $^5\Sigma^+$ electronic states for FeH^+ with $\sigma^3\pi^3\delta^2$ and $\sigma^4\pi^2\delta^2$ electronic configurations, respectively. In 1987 Schilling *et al.*, conducted another theoretical study and provided theoretical evidence for the existence of the $^5\Pi$ and $^5\Sigma^+$ excited states for FeH^+ lying 2.1 and 10.0 kcal mol $^{-1}$ above.⁶ In the same year, Lars *et al.*, carried out modified coupled-pair functional (MCPF) calculations to predict r_e (1.603 Å), ω_e (1805 cm $^{-1}$), and μ (2.41 D) values of $\text{FeH}^+(^5\Delta)$.⁷ They further estimated the D_0 of FeH^+ to be 52.3 kcal mol $^{-1}$, which is 2 kcal mol $^{-1}$ greater than the upper bound of the D_0 reported by Elkind and Armentrout.⁵ Two years later, Sodupe, Lluh, and Oliva studied the PEC originating from the $\text{Fe}^+(^6\text{D}) + \text{H}(^2\text{S})$ fragments using the restricted open Hartree-Fock (ROHF) and configuration interaction levels.⁸ In line with the previous reports, their ROHF calculations predicted a $^5\Delta$ ground state for FeH^+ . However, they found that the inclusion of the electron correlation leads to a $^5\Pi$ ground state for FeH^+ . According to their potential energy profile, all the septet-spin electronic

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† Electronic supplementary information (ESI) available: Fig. S1 illustrates the molecular orbitals of FeH^+ ; Fig. S2 illustrates the μ of $\text{FeH}^+(1^5\Delta)$ under various functionals of DFT; Table S1 lists the total DFT μ of $\text{FeH}^+(1^5\Delta)$ and % DFT errors compared to CCSD(T) μ ; Tables S2 and S3 list the TIPS fit coefficients of FeH^+ and FeH^{2+} ; Table S4 lists the absolute energies of the electronic states of the FeH^+ ; Table S5 lists the absolute energies and the spectroscopic parameters of FeH^+ at CAS(8,7); Table S6 lists the absolute energies of the electronic states of the FeH^{2+} . See DOI: <https://doi.org/10.1039/d4cp03296a>



states originating from the ground state fragments are repulsive in nature. This observation was further corroborated by a study reported by Langhoff and Bauschlicher in 1991.⁹ Specifically, Langhoff and Bauschlicher carried out a theoretical spectroscopic study for FeH^+ utilizing CASSCF (complete active space self-consistent field), MRCI, and MCPDF levels of theory.⁹ The CASSCF order of the states that they observed was $X^5\Delta$, $A^5\Pi$, $B^5\Sigma^+$, $a^3\Sigma^-$, $b^3\Phi$, $c^3\Pi$, and $d^3\Delta$. They reported the MRCI $X^5\Delta \rightarrow A^5\Pi$ and $X^5\Delta \rightarrow a^3\Sigma^-$ transition energies of FeH^+ to be 669 and 10 277 cm^{-1} , respectively. Moreover, their study predicted a D_0 of 50.2 kcal mol^{-1} for FeH^+ . In 2019, Cheng and DeYonker analyzed the low-lying $X^5\Delta$, $A^5\Pi$, $B^5\Sigma^+$, $a^3\Sigma^-$, $b^3\Phi$, $c^3\Pi$, and $d^3\Delta$ states of FeH^+ using MRCI and coupled cluster levels of theories.¹⁰ This is clearly the most complete work reported for FeH^+ so far. Their work utilized a highly accurate focal point approach to calculate the $X^5\Delta \rightarrow A^5\Pi$ (600 cm^{-1}) and $X^5\Delta \rightarrow a^3\Sigma^-$ (10 081 cm^{-1}) transition energies and ionization energy (IE) of FeH (7.4851 eV).¹⁰ Furthermore, this work reported a series of spectroscopic constants for the aforementioned states. The most recent study related to FeH^+ was reported in 2022 by the Beyer group.¹¹ Here they performed infrared multiple photon dissociation (IRMPD) spectroscopic analysis for Ar_2FeH^+ aiming to guide future experimental spectroscopic studies of FeH^+ .

To the best of our knowledge, experimental spectroscopic analysis has not been conducted for FeH^{2+} before. We were only able to locate one WFT based study for this system which was reported by Wilson, Marsden, Nagy-Felsobuki in 2003.¹² This study predicted a $^4\Delta$ ground state for FeH^{2+} with D_e (dissociation energy), r_e , and ω_e values of 21.68 kcal mol^{-1} , 1.998 Å, and 830 cm^{-1} , respectively under the MRCI+Q level of theory.

In the present work we have utilized *ab initio* MRCI^{13–15} method and MRCI+Q¹⁶ correction to analyze the $\text{Fe}^+ + \text{H}$ and $\text{Fe}^{2+} + \text{H}$ reactions and to investigate the ground and electronically excited states of FeH^+ and FeH^{2+} species. The implemented MRCI is indeed capable of providing accurate results for both multireference and single-reference electronic states of highly correlated transition metal-based species such as FeH^+ and FeH^{2+} . Especially, this level of theory is ideal for efficiently producing full PEC for a large number of electronic states of diatomic molecules. On the other hand, the approximate quadruple substitution effect provided by MRCI+Q¹⁶ is often being used to gain more accurate results and reach experimental observations.

Here, we report 27 and 6 MRCI PEC of FeH^+ and FeH^{2+} , respectively. Under MRCI,^{13–15} MRCI+Q,¹⁶ and CCSD(T)¹⁷ levels, their equilibrium electronic configurations, various energy related properties, and a set of spectroscopic parameters are reported. At the MRCI level, the spin-orbit effects of FeH^+ and FeH^{2+} were also evaluated. Furthermore, MRCI DMC and TDMC corresponding to several low-lying electronic states of FeH^+ and FeH^{2+} are introduced. The CCSD(T) μ analyses were also performed for low-lying single-reference electronic states. The μ of the single-reference $\text{FeH}^+(X^5\Delta)$ were also analyzed with 17 functionals that span multiple families of DFA¹⁸ [i.e., semi-local generalized gradient approximation (GGA), meta-GGA (MGGA), global GGA hybrid, MGGA

hybrid, range-separated hybrid (RSH), double hybrid (DH)]. Finally, we used the MRCI PEC of FeH^+ and FeH^{2+} to calculate their TIPS values. We believe that the findings of this work will serve as a guide for future theoretical studies of similar transition metal-based diatomic species and for experimental analysis and identification of FeH^+ and FeH^{2+} in the interstellar space.

II. Computational details

The internally contracted MRCI (\equiv MRCISD)^{13–15} and CCSD(T)¹⁷ calculations were performed using the MOLPRO 2023.2^{19–21} code. First, full MRCI PEC of FeH^+ and FeH^{2+} were produced using the quadruple- ζ quality correlation consistent aug-cc-pVQZ basis set for both atoms.^{22,23} Specifically, the PEC arising from $\text{Fe}^+(^6D) + \text{H}(^2S)$, $\text{Fe}^+(^4F) + \text{H}(^2S)$, $\text{Fe}^+(^4D) + \text{H}(^2S)$, $\text{Fe}^+(^4P) + \text{H}(^2S)$, and $\text{Fe}^+(^2G) + \text{H}(^2S)$ were considered to study the low-lying electronic states of FeH^+ . On the other hand, the PEC of $\text{Fe}^{2+}(^5D) + \text{H}(^2S)$ were analyzed to investigate the electronic states of FeH^{2+} . CASSCF^{24–27} wavefunctions were provided for all MRCI calculations. The CASSCF wave function of FeH^+ were produced by allocating 8 electrons in 12 orbitals [CAS(8,12)]. At the dissociation limit, the active orbitals are the pure atomic orbitals of the five 3d, five 4d, and 4s of Fe and the 1s of H. The same set of orbitals were provided to build CASSCF active space of FeH^{2+} with 7 active electrons [CAS(7,12)]. Under the utilized C_{2v} Abelian point-group, the active orbitals are $6a_1$ ($3d_{z^2}$, $3d_{x^2-y^2}$, $4d_{z^2}$, $4d_{x^2-y^2}$, and 4s of Fe and 1s of H), $2b_1$ ($3d_{xz}$ and $4d_{xz}$ of Fe), $2b_2$ ($3d_{yz}$ and $4d_{yz}$ of Fe), and $2a_2$ ($3d_{xy}$ and $4d_{xy}$ of Fe). At the MRCI level, the single and double electron substitutions from active to virtual orbitals were allowed. The *ad hoc* Davidson correction (MRCI+Q) was applied as a size-extensivity correction.¹⁶ The MRCI and MRCI+Q potential wells of FeH^+ and FeH^{2+} were utilized to solve the rovibrational Schrödinger equation numerically and obtain their harmonic vibrational frequencies (ω_e), anharmonicities ($\omega_e x_e$), equilibrium rotational constants (B_e), anharmonic correction to the rotational constants (α_e), and centrifugal distortion constants (\bar{D}_e). At the MRCI level, DMC and TDMC of several low-lying electronic states of FeH^+ and FeH^{2+} were also produced using the same basis set and active spaces. To evaluate the relativistic effects on the energetics and the spectroscopic constants, potential energy scans were performed at the MRCI and MRCI+Q levels for the 7 and 6 lowest electronic states of FeH^+ and FeH^{2+} , respectively. For these calculations, the aug-cc-pVQZ-DK basis set and the second-order Douglas–Kroll–Hess Hamiltonian were used. Hereafter these calculations are denoted by AQZ-DK-MRCI and AQZ-DK-MRCI+Q. At the AQZ-DK-MRCI level, spin-orbit coupling effects were evaluated by implementing the Breit–Pauli Hamiltonian (more information on the spin-orbit analysis is given in the Discussion section).

The CCSD(T) calculations were performed for a few single-reference electronic states of FeH^+ and FeH^{2+} utilizing the restricted Hartree–Fock (RHF) wave functions. For CCSD(T) calculations, 3 types of correlation consistent basis sets were used: (1) aug-cc-pVQZ/_{Fe,H}, (2) aug-cc-pV5Z/_{Fe,H}, (3) aug-cc-pwCV5Z/_{Fe} aug-cc-pV5Z/_H.^{22,23} Hereafter these CCSD(T) calculations are denoted by AQZ-CCSD(T), A5Z-CCSD(T), and c-A5Z-CCSD(T),



respectively. Note that the $3s^2$ and $3p^6$ core electrons of Fe were correlated at the c-A5Z-CCSD(T).²² The CCSD(T) potential energy scans performed around the equilibrium distance region of the electronic states were utilized to calculate their D_e , r_e , ω_e , $\omega_e x_e$, B_e , α_e , and \bar{D}_e values. Combined with the findings from a previous work of ours, the IE of FeH was calculated at the CCSD(T) level.²⁸ The CCSD(T) μ values of the low-lying single-reference electronic states of FeH^+ and FeH^{2+} were also computed with the finite-field method. For these CCSD(T) μ calculations, a field (f) of 0.01 a.u. was applied to the positive and negative directions of FeH^+ and FeH^{2+} and the calculated $E(f)$ and $E(-f)$ energies were provided for the $\mu = [E(f) - E(-f)]/2f$ equation. The μ of the single-reference $\text{FeH}^+(X^5\Delta)$ was also calculated with DFT using a series of functionals belongs to different families of DFA; semi-local generalized gradient approximation (GGA: BP86,^{29,30} BLYP,^{31,32} PBE³³), meta-GGA (MGGA: TPSS,³⁴ MN15-L³⁵), global GGA hybrid (B3LYP,^{36–38} B3P86,^{29,36} B3PW91,^{36,39} PBE0⁴⁰), MGGA hybrid (TPSSH,³⁴ M06-2X,⁴¹ MN15⁴²), range-separated hybrid (RSH: LRC- ω PBE,⁴³ CAM-B3LYP,⁴⁴ ω B97X⁴⁵), and double hybrid (DH: PBE0-DH,⁴⁶ DSDPBEP86^{47,48}). The DFT μ values were calculated at the previously reported DFT r_e values of $\text{FeH}^+(X^5\Delta)$ combined with the aug-cc-pVQZ basis set.²⁸ In all cases, the default origins (center of the mass) were used for the dipole moment calculations. For DFT calculations, Gaussian 16⁴⁹ software was used.

The TIPS, Q , of a species can be evaluated *via*

$$Q = \sum_j g_j \exp\left(-\frac{E_{j,0}}{k_B T}\right),$$

where g_j is the degeneracy or statistical weight (including the nuclear spin) of level j , k_B is the Boltzmann constant, T is the temperature, and $E_{j,0}$ is the excitation energy of level j from the ground state. For the evaluation of the FeH^+ and FeH^{2+} TIPS, rovibrational energy levels were calculated by solving the rovibrational Schrödinger equation,⁵⁰ where all bound rovibrational levels⁵⁰ within the 27 electronic states of FeH^+ and 6 electronic states of FeH^{2+} were included in the sum.

III. Results and discussion

III.A. FeH^+

The implementation of large active spaces that include additional diffuse type d-functions, rather than traditional valence orbitals-based spaces has been tested to provide more accurate energetics and electronic structures for group 8 transition metal-based diatomic systems (*i.e.*, FeH, FeO^{2+} , RuO^{2+}).^{28,51,52} Similarly, in the current study we have utilized large active spaces that are made of the five 3d, five 4d, and the 4s, atomic orbitals of Fe and the 1s atomic orbital of H for all of our multireference calculations. Using this active space, first we studied several CASSCF PEC of FeH^+ that are originating from various asymptotes of Fe^+ and H.

The ground state of Fe^+ is a 6D with $3d^6 4s^1$ valence electron configuration.⁵³ The transfer of the $4s^1$ electron to 3d orbitals produces its first excited state 4F (at ~ 5.35 – 8.91 kcal mol⁻¹).⁵³ The second excited state of Fe^+ (4D) has an electron arrangement

similar to the ground state, but with a lower spin due to the electron coupling (4D ; at 22.75–25.29 kcal mol⁻¹).⁵³ The next state of Fe^+ is a 4P with $3d^7$ configuration (at 38.53–39.76 kcal mol⁻¹).⁵³ The fourth excited state of Fe^+ is indeed the first doublet-spin electronic state of Fe^+ (2G ; $3d^7$) lying at 45.30–46.80 kcal mol⁻¹.⁵³ The interactions of all these electronic states of Fe^+ with the $\text{H}(^2S)$ ground state were selected to investigate the low-lying electronic states of FeH^+ . The reactions between $\text{Fe}^+(^6D) + \text{H}(^2S)$, $\text{Fe}^+(^4F) + \text{H}(^2S)$, $\text{Fe}^+(^4D) + \text{H}(^2S)$, $\text{Fe}^+(^4P) + \text{H}(^2S)$, and $\text{Fe}^+(^2G) + \text{H}(^2S)$ give rise to $^7,5[\Sigma^+, \Pi, \Delta]$, $^5,3[\Sigma^-, \Pi, \Delta, \Phi]$, $^5,3[\Sigma^+, \Pi, \Delta]$, $^5,3[\Sigma^-, \Pi]$, and $^3,1[\Sigma^+, \Pi, \Delta, \Phi, \Gamma]$ states.^{54,55} We used the CASSCF PEC of the aforementioned asymptotes to identify the lowest energy electronic states of FeH^+ ; specifically its most stable 27 states were studied under the MRCI level of theory. Our calculated MRCI potential energy profile is given in the Fig. 1. Since we did not consider the interaction of excited states of H with the low-lying electronic states of Fe^+ (due to the excitation energy of H atom being significantly higher), the energies of the fragments at the right side of the potential energy profile correspond to the excitation energies of Fe^+ . As expected, at the dissociation limit, the first 4 excitation energies of Fe^+ at the MRCI level are ~ 4 , 22, 37, and 46 kcal mol⁻¹, which are in reasonable agreement with the experimental values.⁵³

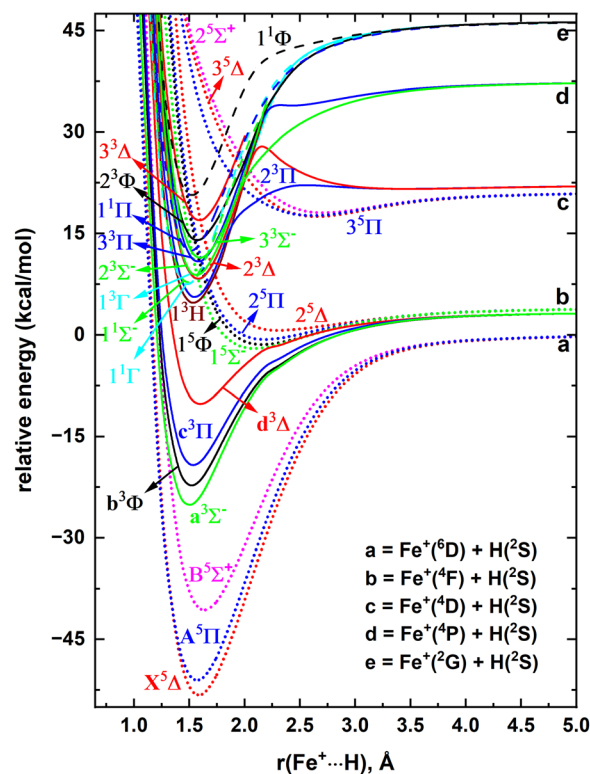


Fig. 1 MRCI/aug-cc-pVQZ PEC of FeH^+ as a function of $\text{Fe}^+\cdots\text{H}$ distance [$r(\text{Fe}^+\cdots\text{H})$, Å]. The relative energies are with respect to the total energy of $\text{Fe}^+(^6D)\cdots\text{H}(^2S)$ when they are at 200 Å separation, which is set to 0 kcal mol⁻¹. The dotted, solid, and dashed PEC correspond to the quintet, triplet, and singlet spins, respectively. The Δ , Π , Σ^+ , Σ^- , Φ , Γ , and H states are shown in red, blue, pink, green, black, cyan, and brown, respectively.



All 3 quintet-spin electronic states originating from the $\text{Fe}^+(\text{}^6\text{D}) + \text{H}(\text{}^2\text{S})$ are strongly attractive and become the first 3 electronic states of FeH^+ (*i.e.*, $\text{X}^5\Delta$, $\text{A}^5\Pi$, and $\text{B}^5\Sigma^+$). Note that within the studied energy range, the septet-spin PEC of the same asymptote are repulsive and do not form minima, and hence are not illustrated in Fig. 1. This is consistent with the previous analysis of the PEC of FeH^+ .^{8,9,56} The next 4 states of FeH^+ are triplet in spin (*i.e.*, $\text{a}^3\Sigma^-$, $\text{b}^3\Phi$, $\text{c}^3\Pi$, $\text{d}^3\Delta$) and dissociate to the second lowest energy asymptote $\text{Fe}^+(\text{}^4\text{F}) + \text{H}(\text{}^2\text{S})$. The quintet-spin states of the same fragments are mildly attractive and form shallow minima around 2–2.3 Å. Interestingly, the ordering of these quintet-spin states (*i.e.*, $1^5\Sigma^-$, $1^5\Phi$, $2^5\Pi$, $2^5\Delta$) of $\text{Fe}^+(\text{}^4\text{F}) + \text{H}(\text{}^2\text{S})$ is the same as the ordering of its triplet-spin states. Beyond this point, the electronic spectrum of FeH^+ is quite complicated with a series of closely arranged electronic states dissociating to $\text{Fe}^+(\text{}^4\text{D}) + \text{H}(\text{}^2\text{S})$, $\text{Fe}^+(\text{}^4\text{P}) + \text{H}(\text{}^2\text{S})$, $\text{Fe}^+(\text{}^2\text{G}) + \text{H}(\text{}^2\text{S})$, and more high energy fragments (Fig. 1).

The equilibrium electronic configurations of the studied 27 electronic states of FeH^+ are reported in the Table 1. The contours of the occupying molecular orbitals are given in ESI† Fig. S1. Notice that the first 3 electronic states of FeH^+ are dominantly single-reference in nature. The $\text{X}^5\Delta$ has the $6\sigma^2 7\sigma^1 3\pi^2 1\delta^3$ configuration and the attachment of an electron to its 7σ orbital produces the dominant electronic configuration of the ground state of FeH ($\text{X}^4\Delta$).²⁸ The first excited state of FeH^+ is formed by transferring an electron from the doubly occupied 1δ orbital to a 3π orbital ($6\sigma^2 7\sigma^1 3\pi^3 1\delta^2$). Similar to the ground state, placing an electron in the singly occupied 7σ of $\text{FeH}^+(\text{}^5\Pi)$ gives rise to the first excited state of FeH ($\text{A}^4\Pi$).²⁸ On the other hand, the electronic structures of $\text{B}^5\Sigma^+$ of FeH^+ and $\text{c}^6\Sigma^+$ of FeH (fifth excited state of FeH) are closely related except for the additional electron occupying in the 8σ of $\text{FeH}(\text{}^6\Sigma^+)$.²⁸ The third excited state of FeH^+ (*i.e.*, $\text{a}^3\Sigma^-$) has a major configuration of $6\sigma^2 3\pi^4 1\delta^2$ but bears a small contribution of $6\sigma^2 3\pi^2 1\delta^4$ as well. The next 3 states are chiefly multi-reference in nature (*i.e.*, $\text{b}^3\Phi$, $\text{c}^3\Pi$, $\text{d}^3\Delta$). Similarly, all other studied states are multi-reference except for the slightly bound $1^5\Sigma^-$ and $2^5\Delta$ states (Table 1 and Fig. 1).

The predominantly single-reference $\text{X}^5\Delta$, $\text{A}^5\Pi$, and $\text{B}^5\Sigma^+$ states of FeH^+ provide us with the opportunity of performing single-reference CCSD(T) calculations for them. The CCSD(T) calculations were performed on top of the RHF wave functions that were produced for their dominant electronic configurations listed in the Table 1. The results of the CCSD(T) calculations carried out with AQZ and A5Z basis sets are listed in the Table 2 along with the AQZ-MRCI and AQZ-MRCI+Q values of FeH^+ . Note that the larger A5Z basis set was only utilized with the CCSD(T) method since CCSD(T) level is relatively less expensive compared to the MRCI level. Furthermore, due to the less demanding nature of CCSD(T) (compared to MRCI), we evaluated the core electron correlation effects on various properties of FeH^+ by unfreezing the $3s^2$ and $3p^6$ core electrons of Fe^+ with the application of proper aug-cc-pwCV5Z basis set of Fe and the results are reported in the Table 2.

The $\text{FeH}^+(\text{}^5\Delta)$ is ~ 8 kcal mol⁻¹ more stable than $\text{FeH}(\text{}^4\Delta)$ [*i.e.*, the adiabatic D_e of $\text{FeH}(\text{}^4\Delta)$ at c-A5Z-CCSD(T) level is

Table 1 Dominant electronic configurations of the 27 electronic states of FeH^+ at their corresponding equilibrium distances

State ^a	Coefficient ^b	Configuration ^c
$\text{X}^5\Delta$ (A ₁)	0.97	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
$\text{A}^5\Pi$ (B ₁)	0.97	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$\text{B}^5\Sigma^+$	0.97	$6\sigma^2 7\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$\text{a}^3\Sigma^-$	0.87	$6\sigma^2 3\pi_x^2 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}$
	-0.31	$6\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
$\text{b}^3\Phi$ (B ₁)	0.65	$6\sigma^2 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.65	$6\sigma^2 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
$\text{c}^3\Pi$ (B ₁)	-0.52	$6\sigma^2 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}$
	0.52	$6\sigma^2 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	-0.49	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$\text{d}^3\Delta$ (A ₁)	0.77	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	-0.34	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	-0.34	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
$1^5\Sigma^-$	0.90	$6\sigma 7\sigma 3\pi_x^2 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.33	$6\sigma 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
$1^5\Phi$ (B ₁)	-0.68	$6\sigma 7\sigma 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.68	$6\sigma 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
$2^5\Pi$ (B ₁)	0.50	$6\sigma 7\sigma 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.50	$6\sigma 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
	0.64	$6\sigma 7\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$2^5\Delta$ (A ₁)	0.93	$6\sigma 7\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
1^3H (B ₁)	0.48	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
	0.48	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2})^2$
	-0.48	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 1\delta_{xy}^2$
	-0.48	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$2^3\Pi$ (B ₁)	0.53	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
	-0.42	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
	0.40	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2})^2$
	0.40	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 1\delta_{xy}$
$1^1\Gamma$ (A ₁)	-0.67	$6\sigma^2 3\pi_x^2 3\pi_y^2 (1\delta_{x^2-y^2})^2$
	0.67	$6\sigma^2 3\pi_x 3\pi_y 1\delta_{xy}$
$1^1\Sigma^-$	0.57	$6\sigma^2 3\pi_x^2 3\pi_y^2 (1\delta_{x^2-y^2})^2$
	0.57	$6\sigma^2 3\pi_x 3\pi_y 1\delta_{xy}$
$1^3\Gamma$ (A ₁)	0.46	$6\sigma^2 7\sigma 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	-0.46	$6\sigma^2 7\sigma 3\pi_x^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	-0.46	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	0.46	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
$2^3\Delta$ (A ₂)	0.68	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.51	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y^2 1\delta_{xy}$
$2^3\Sigma^-$	-0.41	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.41	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.41	$6\sigma^2 7\sigma 3\pi_x^2 (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	-0.41	$6\sigma^2 7\sigma 3\pi_y^2 (1\delta_{x^2-y^2})^2 1\delta_{xy}$
$3^3\Pi$ (B ₁)	0.53	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
	0.53	$6\sigma^2 7\sigma 3\pi_x (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
	-0.31	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$3^3\Sigma^-$	0.57	$6\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}^2$
	-0.40	$6\sigma^2 7\sigma^2 3\pi_x 3\pi_y 1\delta_{xy}^2$
	-0.40	$6\sigma^2 7\sigma^2 3\pi_x 3\pi_y (1\delta_{x^2-y^2})^2$
$1^1\Pi$ (B ₁)	-0.43	$6\sigma^2 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	0.43	$6\sigma^2 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy}$
	0.43	$6\sigma^2 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	-0.43	$6\sigma^2 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
$2^3\Phi$ (B ₁)	0.41	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
	-0.41	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 (1\delta_{x^2-y^2})^2$
	0.41	$6\sigma^2 7\sigma 3\pi_x 3\pi_y^2 1\delta_{xy}$
	-0.41	$6\sigma^2 7\sigma 3\pi_x^2 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$
$3^3\Delta$ (A ₁)	0.47	$6\sigma^2 7\sigma 3\pi_y^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	0.47	$6\sigma^2 7\sigma 3\pi_x^2 (1\delta_{x^2-y^2}) 1\delta_{xy}^2$
	-0.39	$6\sigma^2 7\sigma 3\pi_x 3\pi_y (1\delta_{x^2-y^2}) 1\delta_{xy}$



Table 1 (continued)

State ^a	Coefficient ^b	Configuration ^c
3 ⁵ Δ (A ₁)	0.39	6σ ² 7σ ² 3π _x 3π _y (1δ _{x²-y²)1δ_{xy}}
	0.70	6σ7σ8σ3π _x 3π _y (1δ _{x²-y²)²1δ_{xy}}
3 ⁵ Π (B ₁)	0.32	6σ7σ8σ3π _x 3π _y (1δ _{x²-y²)²1δ_{xy}}
	0.71	6σ7σ8σ3π _x 3π _y ² (1δ _{x²-y²)1δ_{xy}}
2 ⁵ Σ ⁺	0.31	6σ7σ ² 3π _x 3π _y ² (1δ _{x²-y²)1δ_{xy}}
	0.73	6σ ² 7σ8σ3π _x 3π _y (1δ _{x²-y²)1δ_{xy}}
1 ⁴ Φ (B ₁)	0.30	6σ ² 7σ ² 3π _x 3π _y (1δ _{x²-y²)1δ_{xy}}
	0.36	6σ ² 3π _x ² 3π _y (1δ _{x²-y²)²1δ_{xy}}
	-0.36	6σ ² 3π _x ² 3π _y (1δ _{x²-y²)²1δ_{xy}}
	0.36	6σ ² 3π _x 3π _y ² (1δ _{x²-y²)1δ_{xy}²}
	-0.36	6σ ² 3π _x 3π _y ² (1δ _{x²-y²)1δ_{xy}²}

^a The corresponding C_{2v} symmetries of Δ, Π, Φ, Γ, and H are listed in parenthesis. ^b All the CI coefficients that are larger than 0.3 of corresponding natural orbital representations are listed. ^c β and α-spin electrons are specified with and without bars over the spatial orbital, respectively.

46.06 kcal mol⁻¹].²⁸ The AQZ-MRCI level predicted a D_e of 53.27 kcal mol⁻¹ for the FeH⁺(X⁵Δ). MRCI+Q increased the D_e by ~2 kcal mol⁻¹ compared to MRCI. The AQZ-DK-MRCI and AQZ-DK-MRCI+Q D_es are only ~1 kcal mol⁻¹ lower compared to the AQZ-MRCI and AQZ-MRCI+Q for FeH⁺(X⁵Δ). Under all utilized CCSD(T) levels, the D_es of FeH⁺ are ~54 kcal mol⁻¹. The zero-point energy corrected binding energy of FeH⁺ under our largest non-relativistic level of theory c-A5Z-CCSD(T) is 51.79 kcal mol⁻¹. This value is ~1.5 kcal mol⁻¹ greater than the upper bound of the D₀ value of the experimental study by Elkind and Armentrout (*i.e.*, 48.9 ± 1.4 kcal mol⁻¹).⁵ The AQZ-DK-MRCI+Q D₀ is closer to the c-A5Z-CCSD(T) D₀ (*i.e.*, 51.57 versus 51.79 kcal mol⁻¹). The AQZ-DK-MRCI D₀ is 1.95 kcal mol⁻¹ lower compared to the AQZ-DK-MRCI+Q D₀ of FeH⁺(X⁵Δ). Similar to the ground state, all D_es predicted by the 3 CCSD(T) approaches are in between their AQZ-MRCI and AQZ-MRCI+Q values for both A⁵Π and B⁵Σ⁺. Overall, 10 electronic states of FeH⁺ bear positive D_es compared to the ground state fragments [*i.e.*, Fe⁺(⁶D) + H(²S) fragments].

The c-A5Z-CCSD(T) predicted r_e of FeH⁺ (X⁵Δ) is 1.578 Å which is slightly shorter compared to the r_es of core electron correlation disregarded approaches (~1.59 Å). The same pattern was observed for the A⁵Π and B⁵Σ⁺ states as well. The observation of the tendency of core electron correlation to shorten the r_es is in agreement with our past experiences of transition metal-based diatomic species.⁵⁷⁻⁶¹ This is due to the electron excitation from core-to-virtual orbitals which further exposes the nuclear charge of Fe⁺ to a favorable attraction with the valence electron of H. The implementation of relativistic effects decreased the r_es of FeH⁺ slightly. Specifically, the discrepancies between the AQZ-MRCI/AQZ-MRCI+Q versus AQZ-DK-MRCI/AQZ-DK-MRCI+Q are less than 0.03 Å. Among the chemically bound states, the longest r_e was observed for the B⁵Σ⁺ state, which is the only state to host 2 electrons in the 7σ orbital (note: the states with shallow minima are disregarded). The discrepancy between AQZ-MRCI and AQZ-MRCI+Q T_es is less than 570 cm⁻¹ (Table 2). For all states, the AQZ-MRCI+Q predicted T_es are higher than the AQZ-MRCI

(by 230–570 cm⁻¹) except for the first 2 excited state of FeH⁺ in which the AQZ-MRCI+Q predicted 45 and 162 cm⁻¹ lower T_es respectively compared to the AQZ-MRCI. Importantly, both AQZ-MRCI and AQZ-MRCI+Q provided the same ordering for all the electronic states reported in the present work. Among the available relativistic data, the discrepancy between AQZ-DK-MRCI and AQZ-DK-MRCI+Q T_es is less than 400 cm⁻¹.

Overall, our results are in good agreement with the findings reported for the first few states of FeH⁺ by Cheng and DeYonker (Table 2 and ref. 10). The IE of FeH reported by Cheng and DeYonker under a focal point analysis (*i.e.*, 7.4851 eV) is also in good agreement with our adiabatic IEs [*i.e.*, 7.244, 7.263, and 7.425 eV at AQZ-CCSD(T), A5Z-CCSD(T), and c-A5Z-CCSD(T) levels, respectively].¹⁰

The spin-orbit coupling effects of FeH⁺ were evaluated by including the X⁵Δ, A⁵Π, B⁵Σ⁺, a³Σ⁻, b³Φ, c³Π, and d³Δ electronic states of FeH⁺ in the spin-orbit matrix. These electronic states produce Ω = 4, 3, 2, 1, 0⁺, and 0⁻ (X⁵Δ), Ω = 3, 2, 1, 1, 0⁺, and 0⁻ (A⁵Π), Ω = 2, 1, and 0⁺ (B⁵Σ⁺), Ω = 1 and 0⁻ (a³Σ⁻), Ω = 4, 3, and 2 (b³Φ), Ω = 2, 1, 0⁺, and 0⁻ (c³Π), and Ω = 3, 2, and 1 (d³Δ). The spin-orbit curves of these states are depicted in the Fig. 2. Their r_e, T_e, ω_e and ΛS compositions are given in the Table 3. The Ω products of the X⁵Δ span within 0–703 cm⁻¹. The ground spin-orbit state of FeH²⁺ is indeed the Ω = 4 component of the X⁵Δ. The r_e and the ω_e of the Ω = 4 ground state are slightly different from those of the parent X⁵Δ electronic state (Tables 2 and 3). The Ω = 4 ground spin-orbit state is 413 cm⁻¹ more stabilized compared to the X⁵Δ of FeH⁺.

Accurate μ values are vital for calculating radiative characteristics, spectra, and opacities of molecules. Aiming to aid such future studies, here we report MRCI and CCSD(T) μ values of several low-lying electronic states of FeH⁺ (Table 2). Among all states (at equilibrium distances) the largest μ was observed for the ground state of FeH⁺ [~2.3 D at AQZ-MRCI, AQZ-DK-MRCI, and c-A5Z-CCSD(T)] (Table 2). This value is ~0.1 D smaller than the MCPF μ reported by Lars *et al.* in 1987 (*i.e.*, 2.41 D).⁷ The relativistic effects caused a minor change in μ (Table 2). Specifically, the largest difference between AQZ-MRCI versus AQZ-DK-MRCI was observed for the d³Δ state and it is only 0.12 D. Upon comparison of non-relativistic analysis, AQZ-MRCI μ versus c-A5Z-CCSD(T) μ of each X⁵Δ, A⁵Π, and B⁵Σ⁺ are in better agreement and the discrepancies are less than 0.1 D. The AQZ-CCSD(T) and A5Z-CCSD(T) are very close to each other (Table 2) but they are 0.1–0.2 D larger compared to c-A5Z-CCSD(T) μ values.

Here we further report μ of FeH⁺ (X⁵Δ) under a series of exchange correlation functionals that span multiple rungs of Jacob's ladder of DFA aiming to assess its density functional theory errors. Specifically, we used GGAs (BP86,^{29,30} BLYP,^{31,32} PBE³³), MGGAs (TPSS,³⁴ MN15-L³⁵), global GGA hybrids (B3LYP,³⁶⁻³⁸ B3P86,^{29,36} B3PW91,^{36,39} PBE0⁴⁰), MGGAs hybrids (TPSSH,³⁴ M06-2X,⁴¹ MN15⁴²), RSHs (LRC-ωPBE,⁴³ CAM-B3LYP,⁴⁴ ωB97X⁴⁵), and DHs (PBE0-DH,⁴⁶ DSDPBEP86^{47,48}). We utilized the AQZ-CCSD(T) total μ (2.50 D) of FeH⁺ (X⁵Δ) to assess DFT errors since DFT calculations were also performed under the AQZ basis set. We see a general trend of improvement of μ, when moving



Table 2 Adiabatic dissociation energy with respect to the $\text{Fe}^+(\text{}^6\text{D}) + \text{H}(\text{}^2\text{S})$ fragments D_e (kcal mol $^{-1}$), bond length r_e (Å), excitation energy T_e (cm $^{-1}$), harmonic vibrational frequency ω_e (cm $^{-1}$), anharmonicity $\omega_e x_e$ (cm $^{-1}$), equilibrium rotational constant B_e (cm $^{-1}$), anharmonic correction to the rotational constant α_e (cm $^{-1}$), centrifugal distortion constant \bar{D}_e (cm $^{-1}$), and dipole moment (μ) at the equilibrium distance of the 27 low-lying electronic states of FeH^+

State	Level of theory	D_e	r_e	T_e	ω_e	$\omega_e x_e$	B_e	α_e	\bar{D}_e	μ	
$X^5\Delta$	AQZ-MRCI	53.27	1.586	—	1844	34.1	6.765	0.1794	0.000385	−2.31	
	AQZ-MRCI+Q	55.24	1.587	—	1862	30.6	6.758	0.1736	0.000357	—	
	AQZ-DK-MRCI	52.23	1.581	—	1849	34.9	6.818	0.1878	0.000370	−2.26	
	AQZ-DK-MRCI+Q	54.22	1.582	—	1870	32.6	6.802	0.1864	0.000359	—	
	AQZ-CCSD(T)	53.90	1.590	—	1852	30.5	6.752	0.1884	0.000352	−2.50	
	A5Z-CCSD(T)	54.18	1.589	—	1852	30.5	6.743	0.1889	0.000356	−2.50	
	c-A5Z-CCSD(T)	54.44	1.578	—	1865	30.5	6.834	0.1703	0.000365	−2.34	
	MRCI 10		1.5944		1836						
	MRCI+Q 10		1.5891		1848						
	CCSDT 10		1.5882		1850.4	32.2	6.7508	0.1761	0.000359		
	CCSDTQ 10		1.5882		1849.8	32.3	6.7524	0.1765	0.000360		
	FPA 10		1.5736	—	1874.2	31.9	6.8766	0.1798	0.000370		
	$A^5\Pi$	AQZ-MRCI	51.07	1.569	768	1820	34.7	6.906	0.1888	0.000401	−2.14
AQZ-MRCI+Q		53.18	1.570	723	1843	30.9	6.911	0.1852	0.000386	—	
AQZ-DK-MRCI		50.66	1.563	550	1829	33.7	6.974	0.1984	0.000404	−2.08	
AQZ-DK-MRCI+Q		52.77	1.563	507	1857	33.5	6.975	0.1972	0.000396	—	
AQZ-CCSD(T)		51.87	1.575	710	1826	31.1	6.895	0.1755	0.000386	−2.34	
A5Z-CCSD(T)		52.12	1.574	718	1827	31.4	6.878	0.1744	0.000387	−2.34	
c-A5Z-CCSD(T)		52.10	1.564	819	1845	30.8	6.857	0.1784	0.000396	−2.19	
MRCI 10			1.5780		1821						
MRCI+Q 10			1.5711		1837						
CCSDT 10			1.5699		1835.9	32.7	6.9088	0.1861	0.000391		
CCSDTQ 10			1.5697		1835.0	32.8	6.9105	0.1866	0.000392		
FPA 10			1.5558	601	1859.4	31.7	7.0351	0.1898	0.000402		
$B^5\Sigma^+$		AQZ-MRCI	40.69	1.637	4401	1709	37.3	6.347	0.1879	0.000352	−2.23
	AQZ-MRCI+Q	43.12	1.633	4239	1722	32.4	6.389	0.1807	0.000358	—	
	AQZ-DK-MRCI	41.64	1.620	3703	1712	37.7	6.491	0.2052	0.000372	−2.10	
	AQZ-DK-MRCI+Q	44.09	1.615	3540	1750	33.4	6.527	0.2057	0.000363	—	
	AQZ-CCSD(T)	42.75	1.635	3902	1727	33.3	6.368	0.1797	0.000346	−2.48	
	A5Z-CCSD(T)	42.84	1.635	3965	1727	33.4	6.370	0.1820	0.000347	−2.45	
	c-A5Z-CCSD(T)	42.28	1.630	4253	1730	32.7	6.411	0.1838	0.000352	−2.31	
	AQZ-MRCI	25.19	1.497	9821	1938	71.1	7.703	0.4284	0.000624	−1.40	
	AQZ-MRCI+Q	26.34	1.497	10 109	1897	69.7	7.603	0.3068	0.000488	—	
	AQZ-DK-MRCI	20.92	1.489	10 949	1959	61.8	7.680	0.3714	0.000561	−1.49	
	AQZ-DK-MRCI+Q	22.13	1.489	11 223	1974	58.7	7.679	0.3622	0.000547	—	
	MRCI 10		1.4907		1922						
	MRCI+Q 10		1.4944		1901						
CCSDT 10		1.4831		2000.3	47.6	7.7419	0.2522	0.000464			
CCSDTQ 10		1.4862		1977.1	49.6	7.7093	0.2598	0.000469			
FPA 10		1.4821	10 081	1965.0	51.0	7.7530	0.2745	0.000481			
$b^3\Phi$	AQZ-MRCI	22.29	1.517	10 835	1886	92.0	7.515	0.4764	0.000653	−1.34	
	AQZ-MRCI+Q	23.29	1.517	11 175	1844	81.9	7.395	0.4341	0.000475	—	
	AQZ-DK-MRCI	18.22	1.509	11 896	1906	87.4	7.574	0.4006	0.000578	−1.45	
	AQZ-DK-MRCI+Q	19.27	1.509	12 222	1922	84.6	7.566	0.3915	0.000569	—	
	AQZ-MRCI	19.26	1.533	11 896	1824	99.1	7.399	0.5214	0.000635	−1.37	
$c^3\Pi$	AQZ-MRCI+Q	20.30	1.532	12 222	1769	83.4	7.253	0.3544	0.000488	—	
	AQZ-DK-MRCI	15.48	1.520	12 853	1839	92.5	7.473	0.4255	0.000600	−1.46	
	AQZ-DK-MRCI+Q	16.58	1.520	13 162	1866	89.1	7.469	0.4139	0.000599	—	
	AQZ-MRCI	10.21	1.599	15 063	1581	108.0	6.637	0.4950	0.000694	−1.16	
	AQZ-MRCI+Q	11.10	1.598	15 438	1513	97.7	6.670	0.3950	0.000518	—	
$d^3\Delta$	AQZ-DK-MRCI	7.15	1.574	15 765	1617	111.5	6.876	0.5075	0.000712	−1.28	
	AQZ-DK-MRCI+Q	8.13	1.573	16 120	1658	96.3	6.883	0.4891	0.000723	—	
	AQZ-MRCI	2.05	2.079	17 915	—	—	—	—	—	—	
	AQZ-MRCI+Q	2.52	2.061	18 442	—	—	—	—	—	—	
	AQZ-MRCI	1.47	2.149	18 118	—	—	—	—	—	—	
$1^5\Phi$	AQZ-MRCI+Q	1.86	2.133	18 671	—	—	—	—	—	—	
	AQZ-MRCI	0.71	2.171	18 384	—	—	—	—	—	—	
	AQZ-MRCI+Q	1.13	2.149	18 926	—	—	—	—	—	—	
$2^5\Pi$	AQZ-MRCI	—	2.297	18 862	—	—	—	—	—	—	
	AQZ-MRCI+Q	—	2.267	19 424	—	—	—	—	—	—	
	AQZ-MRCI	—	1.534	20 288	1824	66.9	7.399	0.5214	0.000735	—	
1^3H	AQZ-MRCI+Q	—	1.532	20 527	1811	71.5	7.259	0.5462	0.000813	—	
	AQZ-MRCI	—	1.546	20 591	1959	22.4	7.121	0.4947	0.000376	—	
	AQZ-MRCI+Q	—	1.545	21 002	1898	31.4	7.132	0.4183	0.000413	—	
$2^3\Pi$	AQZ-MRCI	—	1.473	21 215	1928	28.0	7.803	0.2190	0.000482	—	
	AQZ-MRCI+Q	—	1.472	21 600	2016	29.7	7.855	0.2223	0.000477	—	
	AQZ-MRCI	—	1.485	21 330	2085	62.2	7.735	0.2492	0.000457	—	



Table 2 (continued)

State	Level of theory	D_e	r_e	T_e	ω_e	$\omega_e x_e$	B_e	α_e	\bar{D}_e	μ
$1^3\Gamma$	AQZ-MRCI+Q	—	1.485	21 722	2014	54.7	7.768	0.2580	0.000463	—
	AQZ-MRCI	—	1.581	21 526	1793	28.9	6.866	0.1694	0.000415	—
$2^3\Delta$	AQZ-MRCI+Q	—	1.580	21 939	1755	30.1	6.825	0.1607	0.000413	—
	AQZ-MRCI	—	1.580	21 540	1746	38.9	6.821	0.2613	0.000406	—
$2^3\Sigma^-$	AQZ-MRCI+Q	—	1.581	21 954	1795	41.9	6.813	0.2814	0.000393	—
	AQZ-MRCI	—	1.562	21 733	1807	31.5	6.892	0.2360	0.000512	—
$3^3\Pi$	AQZ-MRCI+Q	—	1.561	22 114	1801	29.7	6.884	0.1976	0.000489	—
	AQZ-MRCI	—	1.581	22 430	1823	36.0	6.826	0.1877	0.000411	—
$3^3\Sigma^-$	AQZ-MRCI+Q	—	1.580	22 809	1831	36.1	6.839	0.1862	0.000404	—
	AQZ-MRCI	—	1.598	22 629	1769	55.9	6.684	0.2353	0.000326	—
$1^1\Pi$	AQZ-MRCI+Q	—	1.597	22 919	1780	52.5	6.680	0.2188	0.000376	—
	AQZ-MRCI	—	1.508	22 978	1918	46.4	7.482	0.2334	0.000457	—
$2^3\Phi$	AQZ-MRCI+Q	—	1.507	23 379	1924	46.6	7.501	0.2448	0.000456	—
	AQZ-MRCI	—	1.570	23 521	1686	38.6	6.867	0.2403	0.000433	—
$3^3\Delta$	AQZ-MRCI+Q	—	1.568	23 885	1744	36.2	6.839	0.2161	0.000404	—
	AQZ-MRCI	—	1.591	24 552	1761	35.6	6.725	0.1956	0.000392	—
$3^5\Delta$	AQZ-MRCI+Q	—	1.589	24 897	1771	36.5	6.745	0.1960	0.000391	—
	AQZ-MRCI	—	2.649	24 745	—	—	—	—	—	—
$3^5\Pi$	AQZ-MRCI+Q	—	2.603	25 168	—	—	—	—	—	—
	AQZ-MRCI	—	2.613	24 794	—	—	—	—	—	—
$2^5\Sigma^+$	AQZ-MRCI+Q	—	2.569	25 232	—	—	—	—	—	—
	AQZ-MRCI	—	2.707	24 938	—	—	—	—	—	—
$1^1\Phi$	AQZ-MRCI+Q	—	2.678	25 404	—	—	—	—	—	—
	AQZ-MRCI	—	1.522	25 851	1884	28.9	7.311	0.2061	0.000440	—
	AQZ-MRCI+Q	—	1.520	26 242	1831	28.6	7.366	0.2087	0.000440	—

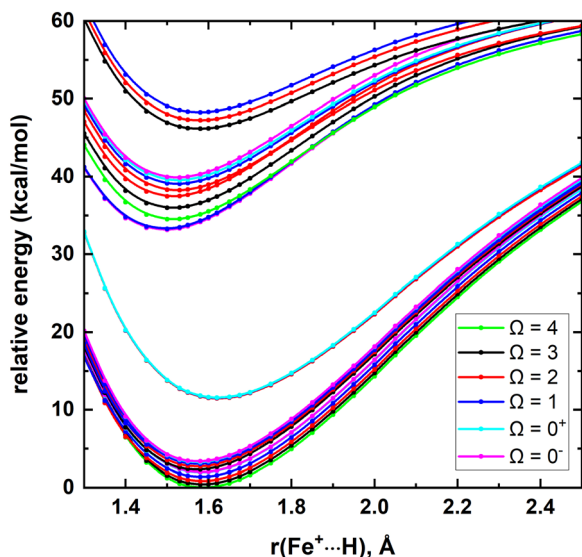


Fig. 2 AQZ-DK-MRCI spin-orbit coupling curves resulting from $X^5\Delta$, $A^5\Pi$, $B^5\Sigma^+$, $a^3\Sigma^-$, $b^3\Phi$, $c^3\Pi$, and $d^3\Delta$ electronic states of FeH^+ as a function of $Fe^+\cdots H$ distance [$r(Fe^+\cdots H)$, Å]. The relative energies are referenced with respect to the $\Omega = 4$ ground state minimum of FeH^+ . The $\Omega = 4$, $\Omega = 3$, $\Omega = 2$, $\Omega = 1$, $\Omega = 0^+$, and $\Omega = 0^-$ curves are shown in green, black, red, blue, cyan, and pink, respectively. See Fig. 1 for the PEC of their parent electronic states.

from lower to higher rungs of DFA (ESI,† Fig. S2 and Table S1). Compared to CCSD(T), the more expensive DHs (PBE0-DH and DSDPBEP86) overestimated μ by ~ 5 and 13% (ESI,† Table S1). All 3 functionals of RSH predicted μ values with less than 9% of errors. The MGGA hybrid M06-2X μ is almost identical to the AQZ-CCSD(T) μ value (2.53 versus 2.50 D) and this is the best

Table 3 Bond length r_e (Å), excitation energy T_e (cm^{-1}), harmonic vibrational frequency ω_e (cm^{-1}), and % ΛS composition of several low-lying spin-orbit states of FeH^+ at AQZ-DK-MRCI level

Ω	r_e	T_e	ω_e	ΛS composition ^a
4	1.586	0	1859	100% $X^5\Delta$
3	1.584	139	1868	89% $X^5\Delta$ + 11% $A^5\Pi$
2	1.583	288	1800	82% $X^5\Delta$ + 18% $A^5\Pi$
1	1.582	479	1797	75% $X^5\Delta$ + 25% $A^5\Pi$
0^+	1.581	688	1792	68% $X^5\Delta$ + 31% $A^5\Pi$
0^-	1.581	703	1794	73% $X^5\Delta$ + 27% $A^5\Pi$
3	1.570	812	1844	89% $A^5\Pi$ + 11% $X^5\Delta$
2	1.572	949	1851	81% $A^5\Pi$ + 18% $X^5\Delta$
1	1.573	1063	1861	76% $A^5\Pi$ + 23% $X^5\Delta$
1	1.568	1130	1784	98% $A^5\Pi$ + 2% $X^5\Delta$
0^+	1.573	1134	1884	67% $A^5\Pi$ + 32% $X^5\Delta$ + 1% $B^5\Sigma^+$
0^-	1.573	1174	1872	73% $A^5\Pi$ + 27% $X^5\Delta$
2	1.623	4005	1725	100% $B^5\Sigma^+$
1	1.622	4033	1724	99% $B^5\Sigma^+$ + 1% $A^5\Pi$
0^+	1.622	4042	1728	98% $B^5\Sigma^+$ + 2% $A^5\Pi$
0^-	1.492	11 577	1930	95% $a^3\Sigma^-$ + 5% $c^3\Pi$
1	1.492	11 628	1938	97% $a^3\Sigma^-$ + 3% $c^3\Pi$
4	1.511	12 060	1893	100% $b^3\Phi$
3	1.511	12 574	1894	100% $b^3\Phi$
2	1.511	13 093	1890	100% $b^3\Phi$
2	1.522	13 366	1828	100% $c^3\Pi$
1	1.522	13 654	1842	96% $c^3\Pi$ + 3% $a^3\Sigma^-$
0^-	1.523	13 818	1834	100% $c^3\Pi$
0^+	1.521	13 941	1847	95% $c^3\Pi$ + 5% $a^3\Sigma^-$
3	1.577	16 136	1627	100% $d^3\Delta$
2	1.577	16 514	1624	99% $d^3\Delta$
1	1.577	16 877	1619	100% $d^3\Delta$

^a Only components that are equal or larger than 1% are listed.

performing functional for μ of $FeH^+(X^5\Delta)$ among all 17 DFAs. The errors of global GGA hybrids span in between 9–17%. The MGGA MN15-L is a clear outlier of the linear-like μ improving trend going from GGA to DHs. However, the MN15-L μ is closer to



the AQZ-CCSD(T) μ than for any functional of GGA. The largest deviation of DFT μ compared to the AQZ-CCSD(T) was observed for the least expensive GGAs with approximate errors of 30% (ESI,† Table S1). Overall, our general expectation that the more expensive functionals from the higher rungs of the Jacob's ladder of DFA would perform better compared to the ones at the lower rungs holds true for the μ of $\text{FeH}^+(\text{X}^5\Delta)$.¹⁸

The DMC of the first 7 electronic states of FeH^+ obtained at the MRCI level are illustrated in the Fig. 3a. Among the focused range, the largest total μ was observed for the $\text{B}^5\Sigma^+$ (2.5 D) around 1.3 Å. The DMC minima of $\text{X}^5\Delta$ and $\text{A}^5\Pi$ were observed at ~ 1.5 Å with -2.4 and -2.2 D, respectively. The DMC of all 4 triplet-spin

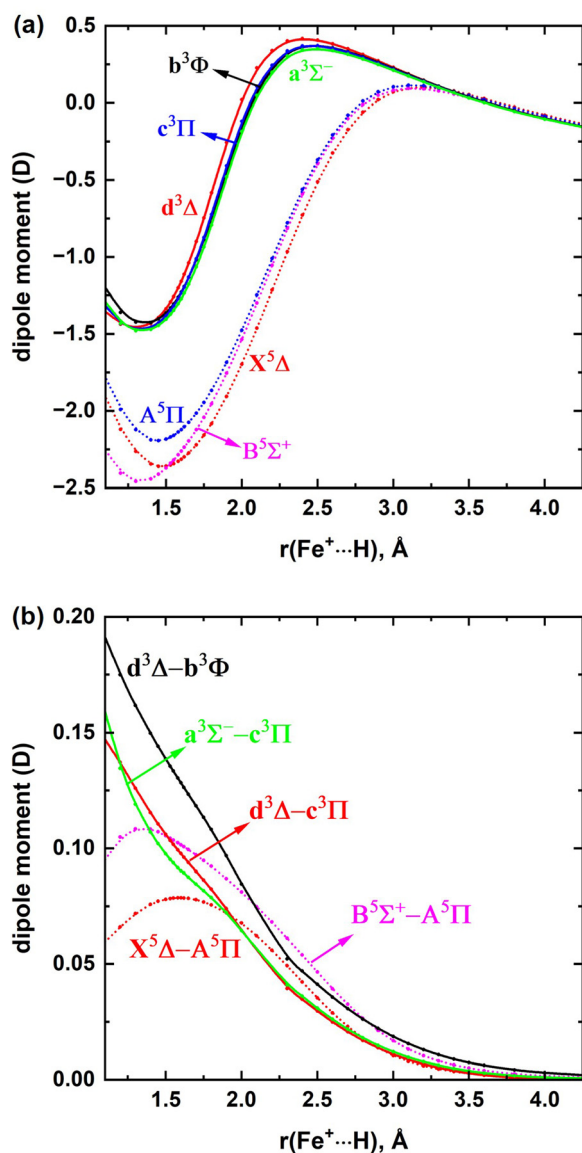


Fig. 3 (a) MRCI/aug-cc-pVQZ DMC of FeH^+ as a function of $\text{Fe}^+\cdots\text{H}$ distance [$r(\text{Fe}^+\cdots\text{H})$, Å]. The solid and dotted DMC correspond to the triplet and quintet spins, respectively. The Δ , Π , Σ^+ , Σ^- , and Φ states are shown in red, blue, pink, green, and black, respectively. (b) MRCI/aug-cc-pVQZ TDMC resulting from $\text{X}^5\Delta \leftrightarrow \text{A}^5\Pi$, $\text{B}^5\Sigma^+ \leftrightarrow \text{A}^5\Pi$, $\text{d}^3\Delta \leftrightarrow \text{c}^3\Pi$, $\text{a}^3\Sigma^- \leftrightarrow \text{c}^3\Pi$, and $\text{d}^3\Delta \leftrightarrow \text{b}^3\Phi$ of FeH^+ as a function of $\text{Fe}^+\cdots\text{H}$ distance [$r(\text{Fe}^+\cdots\text{H})$, Å].

states (*i.e.*, $\text{b}^3\Phi$, $\text{c}^3\Pi$, $\text{d}^3\Delta$, and $\text{a}^3\Sigma^-$) are qualitatively and quantitatively similar throughout the scale and they reach the minimization around the 1.3–1.4 Å. Note that for all states, the DMC minima were observed at slightly shorter $\text{Fe}^+\cdots\text{H}$ distances compared to their equilibrium distances (Fig. 1 and 3). The TDMC arising from the lowest 7 states of FeH^+ are given in Fig. 3b. Among the studied quintet-spin states (*i.e.*, $\text{X}^5\Delta$, $\text{A}^5\Pi$, and $\text{B}^5\Sigma^+$) the $\text{X}^5\Delta \leftrightarrow \text{A}^5\Pi$ and $\text{B}^5\Sigma^+ \leftrightarrow \text{A}^5\Pi$ transitions are permitted, whereas the transition between $\text{X}^5\Delta \leftrightarrow \text{B}^5\Sigma^+$ is forbidden. The largest transition μ values of $\text{X}^5\Delta \leftrightarrow \text{A}^5\Pi$ and $\text{B}^5\Sigma^+ \leftrightarrow \text{A}^5\Pi$ were observed at approximately 1.6 and 1.3 Å and they are only 0.08 and 0.11 D, respectively. The $\text{d}^3\Delta \leftrightarrow \text{c}^3\Pi$, $\text{a}^3\Sigma^- \leftrightarrow \text{c}^3\Pi$, and $\text{d}^3\Delta \leftrightarrow \text{b}^3\Phi$ transitions are allowed for the studied triplet-spin states of FeH^+ and the corresponding transition μ values are increasing with the compression of the $\text{Fe}^+\cdots\text{H}$ distance.

III.B. FeH^{2+}

The removal of the $4s^1$ valence electron from the Fe^+ (^6D ; $[\text{Ar}]3\text{d}^64s^1$) produces the ground electronic state of Fe^{2+} (^5D ; $[\text{Ar}]3\text{d}^6$).⁵³ The low energy electronic spectrum of Fe^{2+} is much less dense compared to the spectrum of Fe^+ . For example, the first excited state of Fe^{2+} (^3P ; $[\text{Ar}]3\text{d}^6$) lies 55.48–60.64 kcal mol⁻¹ above, whereas Fe^+ populates 5 excited states within 0–55 kcal mol⁻¹ range.⁵³ Since the excitation energies of Fe^{2+} are relatively high in energy, in the present work we have only considered the reaction between the ground state of Fe^{2+} (^5D) and $\text{H}(^2\text{S})$. According to the Wigner–Witmer rules, this combination produces $^6,4[\Sigma^+, \Pi, \Delta]$ electronic states. Here all of these states were analyzed under the MRCI level of theory.^{54,55} Similar to FeH^+ , the CASSCF active space used for MRCI calculations of FeH^{2+} was constructed from the

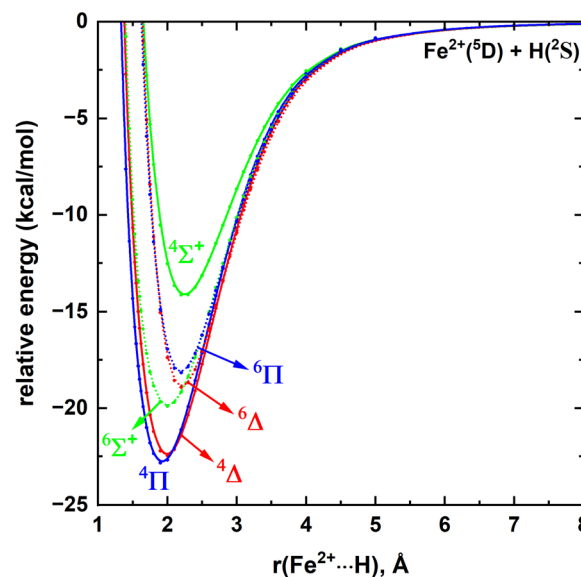


Fig. 4 MRCI/aug-cc-pVQZ PEC of FeH^{2+} as a function of $\text{Fe}^{2+}\cdots\text{H}$ distance [$r(\text{Fe}^{2+}\cdots\text{H})$, Å]. The relative energies are with respect to the total energy of $\text{Fe}^{2+}(^5\text{D}) + \text{H}(^2\text{S})$ when they are at 200 Å separation, which is set to 0 kcal mol⁻¹. The solid and dotted PEC correspond to the quartet and sextet spins, respectively. The Δ , Π , and Σ^+ states are shown in red, blue, and green, respectively.



five 3d, five 4d, and the 4s orbitals of Fe and the 1s orbital of H [CAS(7,12)]. The full PEC of the 6 electronic states of FeH^{2+} studied are given in the Fig. 4.

All PEC are attractive in nature with $\sim 14\text{--}23$ kcal mol $^{-1}$ D_e . According to the MRCI potential energy profile, the ground state of FeH^{2+} is a ${}^4\Pi$ state, followed very closely by a ${}^4\Delta$ state (Fig. 4). The two most stable states of FeH^{2+} (${}^4\Pi$ and ${}^4\Delta$) are

Table 4 Dominant electronic configurations at the equilibrium distances of the 6 low-lying electronic states of FeH^{2+}

State ^a	Coefficient ^b	Configuration ^c
${}^4\Pi$	0.74	$6\sigma^2 3\pi_x^2 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$
	-0.43	$7\sigma^2 3\pi_x^2 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$
${}^4\Delta$	0.73	$6\sigma^2 3\pi_x 3\pi_y(1\delta_{x^2-y^2})^2 1\delta_{xy}$
	-0.44	$7\sigma^2 3\pi_x 3\pi_y(1\delta_{x^2-y^2})^2 1\delta_{xy}$
${}^6\Sigma^+$	0.99	$6\sigma^2 7\sigma 3\pi_x 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$
${}^6\Delta$	0.99	$6\sigma 7\sigma 3\pi_x 3\pi_y(1\delta_{x^2-y^2})^2 1\delta_{xy}$
${}^6\Pi$	0.99	$6\sigma 7\sigma 3\pi_x^2 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$
${}^4\Sigma^+$	0.83	$6\sigma^2 7\sigma 3\pi_x 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$
	-0.32	$6\sigma 7\sigma^2 3\pi_x 3\pi_y(1\delta_{x^2-y^2})1\delta_{xy}$

^a The corresponding A_1 (of Δ) and B_1 (of Π) components under C_{2v} symmetry are listed. ^b All the CI coefficients that are larger than 0.3 of corresponding natural orbital representations are given. ^c β and α -spin electrons are specified with and without bars over the spatial orbital, respectively.

multireference in nature (Table 4). The electronic configurations of the two main components of the ${}^4\Pi$ state are $6\sigma^2 3\pi^3 1\delta^2$ (55%) and $7\sigma^2 3\pi^3 1\delta^2$ (18%). Notice that the major configuration of ${}^4\Pi$ state ($6\sigma^2 3\pi^3 1\delta^2$) can be produced by eliminating the $7\sigma^1$ electron from the $A^5\Pi$ of FeH^+ ($6\sigma^2 7\sigma^1 3\pi^3 1\delta^2$). The MRCI and MRCI+Q predicted IEs of this process are 17.0 and 17.2 eV, respectively. On the other hand, the dominant configuration of the ${}^4\Delta$ ($6\sigma^2 3\pi^2 1\delta^3$) is the $7\sigma^1$ electron ionized product of the FeH^+ ($X^5\Delta$; $6\sigma^2 7\sigma^1 3\pi^2 1\delta^3$). The next 3 states of FeH^{2+} carry single-reference electronic configurations and hence those were further analyzed with CCSD(T) levels of theory. All our CCSD(T) and MRCI numerical findings of FeH^{2+} are listed in Table 5.

The D_e of $\text{FeH}^{2+}({}^4\Pi)$ under AQZ-MRCI and AQZ-MRCI+Q levels are 22.85 and 23.13 kcal mol $^{-1}$. The zero-point energy corrected AQZ-MRCI and AQZ-MRCI+Q D_0 s of $\text{FeH}({}^4\Pi)$ are 21.66 and 21.94 kcal mol $^{-1}$. Under both AQZ-MRCI and AQZ-MRCI+Q levels the ${}^4\Delta$ state lies only 0.4 kcal mol $^{-1}$ above the ${}^4\Pi$ (Table 5) (*i.e.*, the AQZ-MRCI and AQZ-MRCI+Q D_0 of ${}^4\Delta$ are 21.29 and 21.49, respectively). Our MRCI+Q is only 1 kcal mol $^{-1}$ larger than the MRCI+Q D_e of ${}^4\Delta$ reported by Wilson *et al.* in 2003 (22.68 *versus* 21.68 kcal mol $^{-1}$).¹² Our AQZ-DK-MRCI and AQZ-DK-MRCI+Q D_0 values of $\text{FeH}^{2+}({}^4\Pi)$ are 22.27 and 22.57 kcal mol $^{-1}$, respectively. The introduction of the relativistic effects only increased the D_0 of $\text{FeH}^{2+}({}^4\Pi)$ by ~ 1 kcal mol $^{-1}$.

Table 5 Adiabatic dissociation energy with respect to the $\text{Fe}^{2+}({}^5D) + \text{H}({}^2S)$ fragments D_e (kcal mol $^{-1}$), bond length r_e (Å), excitation energy T_e (cm $^{-1}$), harmonic vibrational frequency ω_e (cm $^{-1}$), anharmonicity $\omega_e x_e$ (cm $^{-1}$), equilibrium rotational constant B_e (cm $^{-1}$), anharmonic correction to the rotational constant α_e (cm $^{-1}$), centrifugal distortion constant \bar{D}_e (cm $^{-1}$), and dipole moment (μ) at equilibrium distance of the 6 low-lying electronic states of FeH^{2+}

State	Level of theory	D_e	r_e	T_e	ω_e	$\omega_e x_e$	B_e	α_e	\bar{D}_e	μ
${}^4\Pi$	AQZ-MRCI	22.85	1.923	—	841	16.3	4.604	0.1566	0.000552	1.21
	AQZ-MRCI+Q	23.13	1.918	—	846	16.2	4.639	0.1574	0.000529	—
	AQZ-DK-MRCI	23.47	1.908	—	848	15.8	4.690	0.1566	0.000538	1.22
	AQZ-DK-MRCI+Q	23.76	1.902	—	852	15.7	4.711	0.1157	0.000562	—
${}^4\Delta$	AQZ-MRCI	22.47	1.989	135	839	17.0	4.314	0.1369	0.000455	1.36
	AQZ-MRCI+Q	22.68	1.986	156	841	17.0	4.329	0.1367	0.000453	—
	AQZ-DK-MRCI	22.95	1.977	180	842	16.5	4.368	0.1366	0.000450	1.36
	AQZ-DK-MRCI+Q	23.18	1.973	203	845	16.5	4.384	0.1364	0.000467	—
	MRCI+Q ¹²	21.68	1.998	—	830	—	—	—	—	—
	AQZ-MRCI	19.90	1.999	1033	719	4.9	4.263	0.1503	0.000567	1.15
	AQZ-MRCI+Q	20.15	1.994	1042	727	4.4	4.297	0.1512	0.000574	—
${}^6\Sigma^+$	AQZ-DK-MRCI	21.60	1.913	654	712	11.1	4.585	0.2079	0.000768	1.05
	AQZ-DK-MRCI+Q	21.89	1.909	653	719	14.3	4.675	0.2141	0.000781	—
	AQZ-CCSD(T)	19.95	2.016	—	728	6.1	4.195	0.1144	0.000582	1.20
	A5Z-CCSD(T)	19.95	2.018	—	734	6.2	4.186	0.1129	0.000582	1.21
	c-A5Z-CCSD(T)	20.84	2.005	—	747	5.6	4.240	0.1225	0.000539	1.25
	AQZ-MRCI	18.92	2.203	1376	836	21.3	3.514	0.1370	0.000247	1.38
	AQZ-MRCI+Q	19.04	2.202	1430	836	21.2	3.516	0.1337	0.000248	—
	AQZ-DK-MRCI	19.64	2.190	1339	891	26.3	3.551	0.1180	0.000225	1.40
	AQZ-DK-MRCI+Q	19.77	2.197	1396	887	26.3	3.630	0.1129	0.000223	—
	AQZ-CCSD(T)	19.06	2.202	—	837	22.6	3.512	0.1350	0.000287	1.42
${}^6\Delta$	A5Z-CCSD(T)	19.07	2.202	—	837	22.5	3.513	0.1343	0.000262	1.42
	c-A5Z-CCSD(T)	20.01	2.188	—	850	22.2	3.556	0.1331	0.000258	1.48
	AQZ-MRCI	18.17	2.187	1638	819	21.7	3.560	0.1428	0.000246	1.34
	AQZ-MRCI+Q	18.31	2.185	1687	820	21.2	3.570	0.1405	0.000269	—
	AQZ-DK-MRCI	18.96	2.171	1575	834	21.8	3.613	0.1375	0.000270	1.38
	AQZ-DK-MRCI+Q	19.11	2.169	1624	832	21.0	3.618	0.1144	0.000275	—
	AQZ-CCSD(T)	18.33	2.186	—	821	22.7	3.562	0.1404	0.000274	1.40
	A5Z-CCSD(T)	18.35	2.186	—	821	22.6	3.563	0.1391	0.000246	1.40
	c-A5Z-CCSD(T)	19.21	2.173	—	833	22.3	3.601	0.1372	0.000247	1.37
	AQZ-MRCI	14.18	2.246	3031	712	22.4	3.388	0.1484	0.000315	1.17
${}^4\Sigma^+$	AQZ-MRCI+Q	14.34	2.242	3073	716	22.1	3.389	0.1460	0.000309	—
	AQZ-DK-MRCI	14.72	2.225	3060	719	21.2	3.450	0.1450	0.000324	1.22
	AQZ-DK-MRCI+Q	14.89	2.220	3101	724	21.4	3.465	0.1448	0.000325	—



Importantly, since the energy difference between the $^4\Pi$ and $^4\Delta$ states is within the margin of error of the basis set and the method, it is difficult to assign a true ground state for FeH^{2+} . We performed AQZ-CCSD(T), A5Z-CCSD(T), and c-A5Z-CCSD(T) calculations for the single-reference $^6\Sigma^+$, $^6\Delta$, and $^6\Pi$ states of FeH^{2+} . For all these 3 states, the AQZ-CCSD(T) $D_{e,s}$ and A5Z-CCSD(T) $D_{e,s}$ are almost identical to each other (Table 5). As expected, the electron excitation from core-to-virtual orbitals [*i.e.*, c-A5Z-CCSD(T)] relaxes (or stabilizes) the electronic states increasing the D_e values approximately by 0.9 kcal mol $^{-1}$. The bond lengths of the electronic states of FeH^{2+} are significantly longer compared to the $r_{e,s}$ of the states of FeH^+ which translate to the lower $D_{e,s}$ of FeH^{2+} compared to FeH^+ (compare $r_{e,s}$ and $D_{e,s}$ given in Tables 2 and 5). This also means that an apparent measured IE of FeH^+ will likely be at higher energies (due to the Franck–Condon overlap). The MRCI+Q r_e of the $^4\Delta$ state reported by Wilson *et al.*, is 0.01 Å longer compared to our MRCI+Q value.¹² For all states, MRCI+Q predicted slightly shorter $r_{e,s}$ compared to MRCI (by ~ 0.001 – 0.005 Å). Similar to the FeH^+ case, the relativistic effects on the $r_{e,s}$ of the states of the FeH^{2+} are minor (Table 5). The c-A5Z-CCSD(T) $r_{e,s}$ of FeH^{2+} are shorter compared to the A5Z-CCSD(T) $r_{e,s}$ similar to the FeH^+ case. The AQZ-MRCI+Q predicted slightly higher $T_{e,s}$ compared to the AQZ-MRCI $T_{e,s}$ (0–60 cm $^{-1}$). The largest discrepancy between the AQZ-DK-MRCI/AQZ-DK-MRCI+Q versus AQZ-MRCI/AQZ-MRCI+Q was observed for the $^6\Sigma^+$ state which is ~ 400 cm $^{-1}$, whereas in all other cases it is less than 65 cm $^{-1}$. Finally, we observed that all AQZ-MRCI+Q, AQZ-MRCI, AQZ-DK-MRCI, and AQZ-DK-MRCI+Q levels' predictions on spectroscopic constants agree well with each other (*i.e.*, ω_e , $\omega_e x_e$, B_e , α_e , and \bar{D}_e).

To investigate the spin–orbit effects of FeH^{2+} , we have included $^4\Pi$, $^4\Delta$, $^6\Sigma^+$, $^6\Delta$, $^6\Pi$, and $^4\Sigma^+$ electronic states in the spin–orbit matrix. The spin–orbit coupling produces the $\Omega = 1/2$, $1/2$, $3/2$, and $5/2$ (from $^4\Pi$), $\Omega = 1/2$, $3/2$, $5/2$, and $7/2$ (from $^4\Delta$), $\Omega = 1/2$, $3/2$, and $5/2$ (from $^6\Sigma^+$), $\Omega = 1/2$, $1/2$, $3/2$, $5/2$, $7/2$, and $9/2$ (from $^6\Delta$), $\Omega = 1/2$, $1/2$, $3/2$, $3/2$, $5/2$, and $7/2$ (from $^6\Pi$), and $\Omega = 1/2$ and $3/2$ (from $^4\Sigma^+$). The spin–orbit curves of the Ω states are given in the Fig. 5 and the corresponding r_e , T_e , ω_e , and ΛS compositions are listed in the Table 6. The Ω states of the ground $^4\Pi$ electronic states span within 0–525 cm $^{-1}$ whereas those of the first excited $^4\Delta$ extend from 150 to 1021 cm $^{-1}$. The ground spin–orbit state of the FeH^{2+} is an $\Omega = 5/2$ which is stabilized over its parent $^4\Pi$ state by 353 cm $^{-1}$. As expected, the $\Omega = 5/2$ ground spin–orbit state bears substantial composition of $^4\Delta$ (20%) due to the proximity of the $^4\Pi$ and $^4\Delta$ states. Similarly, notable mixings were observed for many Ω states which clearly highlights the importance of the spin–orbit coupling effects of the FeH^{2+} system (Table 6).

The AQZ-MRCI and AQZ-DK-MRCI μ values of the $^4\Pi$ and $^4\Delta$ states at their $r_{e,s}$ are 1.2 and 1.4 D, respectively. Among all states, the largest and smallest μ values were observed for the $^6\Delta$ and $^6\Sigma^+$ states, respectively (Table 5). The relativistic effects on the μ values of FeH^{2+} are minor, where the largest difference was observed for the $^6\Sigma^+$ state which is only 0.1 D. Similar to the FeH^+ case, the μ values predicted by AQZ-CCSD(T) levels are

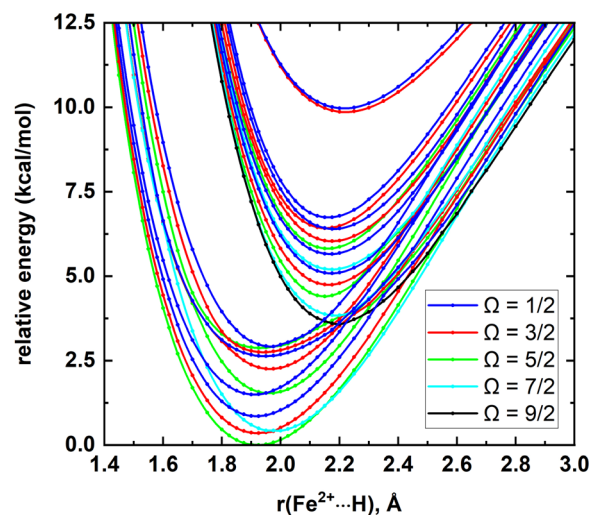


Fig. 5 AQZ-DK-MRCI spin–orbit coupling curves resulting from $^4\Pi$, $^4\Delta$, $^6\Sigma^+$, $^6\Delta$, $^6\Pi$, and $^4\Sigma^+$ electronic states of FeH^{2+} as a function of $\text{Fe}^{2+}\cdots\text{H}$ distance [$r(\text{Fe}^{2+}\cdots\text{H})$, Å]. The relative energies are referenced with respect to the $\Omega = 5/2$ ground state minimum of FeH^{2+} . The $\Omega = 1/2$, $\Omega = 3/2$, $\Omega = 5/2$, $\Omega = 7/2$, and $\Omega = 9/2$ curves are shown in blue, red, green, cyan, and black, respectively. See Fig. 4 for the PEC of their parent $^4\Pi$, $^4\Delta$, $^6\Sigma^+$, $^6\Delta$, $^6\Pi$, and $^4\Sigma^+$ states.

Table 6 Bond length r_e (Å), excitation energy T_e (cm $^{-1}$), harmonic vibrational frequency ω_e (cm $^{-1}$), and % ΛS composition of several low-lying spin–orbit states of FeH^{2+} at AQZ-DK-MRCI level

Ω	r_e	T_e	ω_e	ΛS composition ^a
5/2	1.922	0	810	78% $^4\Pi$ + 20% $^4\Delta$ + 2% $^6\Sigma^+$
3/2	1.919	123	823	82% $^4\Pi$ + 16% $^4\Delta$ + 2% $^6\Sigma^+$
7/2	1.958	150	858	100% $^4\Delta$
1/2	1.917	299	808	88% $^4\Pi$ + 10% $^4\Delta$ + 2% $^6\Sigma^+$
1/2	1.909	524	867	98% $^4\Pi$ + 2% $^6\Sigma^+$
5/2	1.966	538	913	72% $^4\Delta$ + 25% $^4\Pi$ + 3% $^6\Sigma^+$
3/2	1.964	789	833	75% $^4\Delta$ + 17% $^4\Pi$ + 8% $^6\Sigma^+$
1/2	1.947	921	626	85% $^6\Sigma^+$ + 9% $^4\Delta$ + 5% $^6\Pi$
3/2	1.942	964	724	85% $^6\Sigma^+$ + 6% $^4\Pi$ + 5% $^6\Pi$ + 4% $^4\Delta$
5/2	1.929	1007	675	93% $^6\Sigma^+$ + 4% $^4\Pi$ + 2% $^6\Pi$
1/2	1.967	1021	862	79% $^4\Delta$ + 14% $^4\Pi$ + 6% $^6\Sigma^+$
9/2	2.197	1250	904	100% $^6\Delta$
7/2	2.187	1341	916	80% $^6\Delta$ + 20% $^6\Pi$
5/2	2.150	1539	1031	65% $^6\Delta$ + 23% $^6\Sigma^+$ + 10% $^6\Pi$ + 1% $^4\Pi$
3/2	2.164	1659	917	64% $^6\Delta$ + 23% $^6\Pi$ + 12% $^6\Sigma^+$ + 1% $^4\Pi$
1/2	2.173	1778	896	53% $^6\Delta$ + 42% $^6\Pi$ + 4% $^6\Sigma^+$ + 1% $^4\Pi$
7/2	2.174	1818	825	78% $^6\Pi$ + 21% $^6\Delta$ + 1% $^4\Delta$
1/2	2.169	1978	869	61% $^6\Delta$ + 30% $^6\Pi$ + 8% $^6\Sigma^+$ + 1% $^4\Pi$
5/2	2.161	2035	924	66% $^6\Pi$ + 23% $^6\Delta$ + 10% $^6\Sigma^+$ + 1% $^4\Delta$
3/2	2.174	2112	822	76% $^6\Pi$ + 22% $^6\Delta$
1/2	2.179	2238	743	53% $^6\Pi$ + 45% $^6\Delta$ + 2% $^6\Sigma^+$
3/2	2.153	2247	826	77% $^6\Pi$ + 15% $^6\Sigma^+$ + 8% $^6\Delta$
1/2	2.162	2358	830	57% $^6\Pi$ + 31% $^6\Delta$ + 11% $^6\Sigma^+$
3/2	2.220	3449	667	98% $^4\Sigma^+$ + 1% $^6\Pi$ + 1% $^4\Pi$
1/2	2.215	3487	732	97% $^4\Sigma^+$ + 3% $^4\Pi$

^a Only components that are equal or larger than 1% are listed.

larger than the AQZ-MRCI μ . The calculated AQZ-MRCI DMC of the 6 low-lying states of FeH^{2+} are shown in Fig. 6a. Similar to FeH^+ , the μ values of FeH^{2+} increase moving to shorter internuclear distances and shift towards the negative direction. The



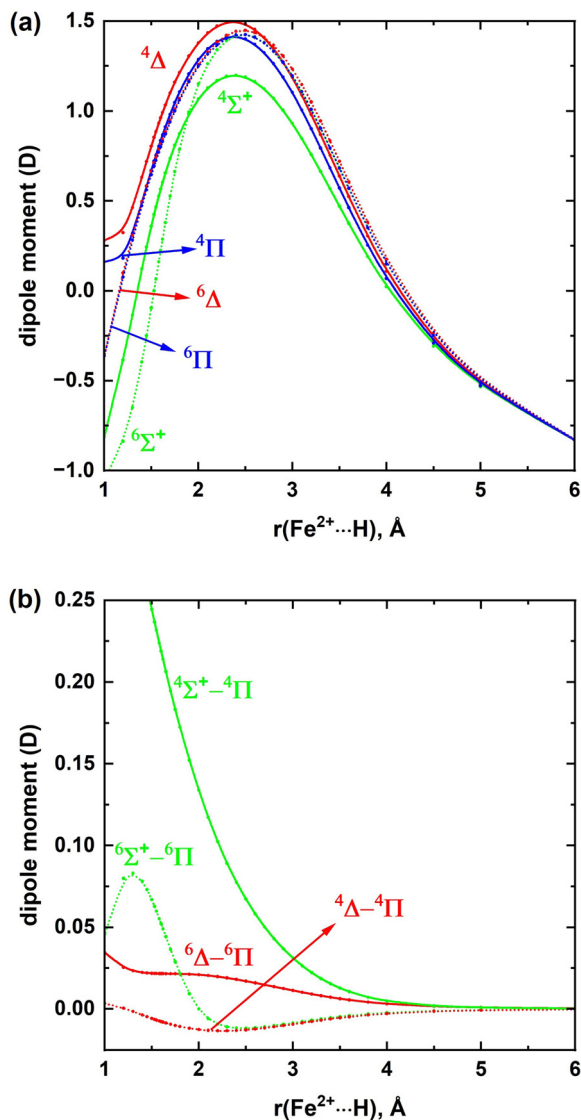


Fig. 6 (a) AQZ-MRCI DMC of FeH^{2+} as a function of $\text{Fe}^{2+}\cdots\text{H}$ distance $[r(\text{Fe}^{2+}\cdots\text{H}), \text{\AA}]$. The solid and dotted DMC correspond to the quartet and sextet spins, respectively. The Δ , Π , and Σ^+ states are shown in red, blue, and green, respectively. (b) AQZ-MRCI TDMC resulting from ${}^4\Delta \leftrightarrow {}^4\Pi$, ${}^6\Delta \leftrightarrow {}^6\Pi$, ${}^6\Sigma^+ \leftrightarrow {}^6\Pi$, and ${}^4\Sigma^+ \leftrightarrow {}^4\Pi$ of FeH^{2+} as a function of $\text{Fe}^{2+}\cdots\text{H}$ distance $[r(\text{Fe}^{2+}\cdots\text{H}), \text{\AA}]$.

maxima of the DMC were observed around the 2.4–2.5 Å. Only ${}^4\Delta \leftrightarrow {}^4\Pi$, ${}^6\Delta \leftrightarrow {}^6\Pi$, ${}^6\Sigma^+ \leftrightarrow {}^6\Pi$, and ${}^4\Sigma^+ \leftrightarrow {}^4\Pi$ transitions are allowed for the studied states of FeH^{2+} . The TDMC corresponding to these transitions are illustrated in the Fig. 6b. Among these transitions, the smallest transition μ values were observed for the $\Delta \leftrightarrow \Pi$. Comparatively, the $\Sigma^+ \leftrightarrow \Pi$ transition μ values are significant. Especially, the ${}^4\Sigma^+ \leftrightarrow {}^4\Pi$ transition μ values increase exponentially moving to shorter internuclear distances.

III.C. TIPS of FeH^+ and FeH^{2+}

In the TIPS calculations of the of FeH^+ and FeH^{2+} , we included all bound rovibrational levels⁵⁰ that were allowed from the respective PEC (see Fig. 1 and 4). Here the FeH^+ $3^3\Sigma^-$, 1^3H ,

and $3^3\Delta$ PEC were extrapolated by fitting each PEC with an extended Morse PEC, noting that these states are products of the $\text{Fe}^+(\text{a}^2\text{H}) + \text{H}(\text{2S})$ reaction. For the states included within the FeH^+ and FeH^{2+} models, we estimate that the present TIPS results are accurate (within $\sim 0.05\%$) up to approximately 5000 K and 1000 K, respectively. However, the errors associated with the accuracy of the PEC and solution of the rovibrational Schrödinger equation are not taken into account. We expect that the present TIPS calculation will have reasonable errors at low temperatures $\lesssim 1500$ K, where the accuracy of the method, spin–orbit coupling and non-adiabatic effects can be relatively important to the TIPS. This is the first presentation of the FeH^+ and FeH^{2+} TIPS in the literature, hence we provide results for the TIPS beyond the expected range of accuracy.

The following TIPS fit function⁶²

$$\log_{10}(Q) = \sum_{n=1}^{N-1} a_n \left[\log_{10} \left(\frac{5040 \text{ K}}{T + a_0} \right) \right]^{n-1},$$

can represent the TIPS over the temperature range 10–30 000 K (and perhaps even over a broader range). The a coefficients were optimized to minimize the maximum error of the fit function, noting that we fit the TIPS over a broader range of temperatures than we expect the TIPS to be accurate for in equations of state calculations. The FeH^+ and FeH^{2+} $N = 17$ and $N = 19$ fit coefficients are given in ESI,[†] Tables S2 and S3, where the errors of the fit functions are less than approximately 0.06% and 0.07%, respectively over the 10–30 000 K range. Note this error is only due to the fit (see above).

IV. Conclusions

The MRCI and CCSD(T) WFT calculations were performed with large correlation consistent basis sets to analyze the ground and excited electronic states of FeH^+ and FeH^{2+} . Multireference calculations were constructed using a bigger active space made of the five 3d, five 4d, and the 4s atomic orbitals of Fe and the 1s atomic orbital of H. We introduced 27 and 6 MRCI PEC for FeH^+ and FeH^{2+} , respectively. The ω_e , $\omega_e x_e$, B_e , α_e , \bar{D}_e spectroscopic parameters and r_e , T_e , and μ values of FeH^+ and FeH^{2+} were obtained using the CCSD(T), MRCI, and MRCI+Q levels of theory. At the MRCI level, spin–orbit coupling effect of FeH^+ and FeH^{2+} were also tested. FeH^+ has 10 bound electronic states with respect to the $\text{Fe}^+(\text{6D}) + \text{H}(\text{2S})$ fragments, but 3 of them are relatively weakly bound with less than 3 kcal mol⁻¹ D_e . The ground state of FeH^+ is a $X^5\Delta$ with a D_0 51.8 kcal mol⁻¹. This value is in reasonable agreement with the previously reported experimental D_0 value of FeH^+ (*i.e.*, 48.9 ± 1.4 kcal mol⁻¹). The $\text{FeH}^+(X^5\Delta)$ bears the $6\sigma^2 7\sigma^1 3\pi^2 1\delta^3$ electronic configuration which can be produced by ionizing an electron from the $7\sigma^2$ of the dominant configuration of the $\text{FeH}(X^4\Delta)$. The calculated IE of this process is 7.425 eV. Among the studied electronic states, the largest μ was observed for the ground state of $\text{FeH}^+(X^5\Delta)$. For all states we observed a good agreement between AQZ-MRCI μ versus c-A5Z-CCSD(T) μ . The μ values of single-reference $\text{FeH}^+(X^5\Delta)$ were calculated with a series of



functionals that span multiple rungs of Jacob's ladder of DFA and compared with the highly reliable CCSD(T) value obtained with the finite-field method. In agreement with our expectation, we observed a general trend of improving μ going from lower to higher rungs of Jacob's ladder of DFA. Furthermore, we introduced the MRCI DMC and TDMC corresponding to several low-lying electronic states of FeH^+ and FeH^{2+} . Compared to the $\text{FeH}^+(X^5\Delta)$, the $\text{FeH}^{2+}(^4\Pi)$ is ~ 30 kcal mol $^{-1}$ less strongly bound. The two most stable electronic states of FeH^{2+} (*i.e.*, $^4\Pi$ and $^4\Delta$) are multireference in nature and bound by ~ 23 kcal mol $^{-1}$ with respect to $\text{Fe}^{2+}(^5D) + \text{H}(^2S)$ dissociation. Lower μ values were observed for the low-lying electronic states of FeH^{2+} compared to those of FeH^+ . The transition μ values for both FeH^+ and FeH^{2+} are relatively small and hence we expect those transitions to produce weak bands in the corresponding spectra. Finally, we provided a fit function and coefficients for calculation of the FeH^+ and FeH^{2+} TIPS. These are the only available TIPS data in the literature for these molecules.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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