Ab Initio Study of Molecular and Electronic Structures of Early Transition Metal Trihydrides MH_3 (M = Sc, Ti, V, Fe)

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Ab initio calculations with accounting for electronic correlation were carried out for ScH_3, VH_3, TiH_3, and FeH_3. Relative energies of excited states of the molecules were evaluated by the equation-of-motion coupled cluster method in the single and double approximation (EOM-CCSD) and ground-state properties were calculated at coupled cluster singles doubles level augmented by pertrubative correction for connected triple excitation (CCSD(T)). The ground electronic states of the molecules were found to have high-spin and planar (D_{3h}) equilibrium geometries. The molecules TiH_3 and VH_3 possess low-lying degenerate electronic states. However, the Jahn−Teller distortion of these states was investigated and found to be small. Correlation corrections to equilibrium internuclear distances, harmonic vibrational frequencies, and infrared intensities are shown to be significant. A comparison of theoretical and available experimental data on the molecules was performed.

1. Introduction

The electronic and molecular structures of first-row transition metal hydrides have been the subject of numerous theoretical and experimental studies, but only a few of these have dealt with the trihydrides.[1−8] The ESR spectra of chromium and manganese trihydrides were studied by Van Zee et al.[2,3] The bands in the infrared spectra of M + H_2 (M = Ti, Fe) systems in an Ar matrix, which were assigned to TiH_3 and FeH_3 molecule, were found by Chertihin et al.[6,7] Xiao et al.[5] reported a similar band, which corresponds to the CrH_3 molecule in the IR spectrum of the Cr + H_2 system in Ar and Kr matrixes. The spectroscopic data were interpreted under the assumption that the molecules have planar (D_{3h}) structures. Chertihin et al.[6] also performed ab initio UHF calculations of the structure and vibrational spectra of TiH_3 that support this suggestion. The molecule ScH_3 was examined only theoretically.[1,4,8] Using the FSGO method, Talaty et al.[1] found ScH_3 to be planar (D_{3h}). In contrast, RHF and MP2 calculations by Jolly and Marynick[4] predicted a pyramidal (C_{3v}) structure for ScH_3 with a high value for the inversion barrier. However, this result has now been reported as erroneous.[9] In the work by Neuhaus et al.[8] (RHF and CASSCF calculations), ScH_3 is reported to be planar (D_{3h}). The calculations by Talaty et al.[1] found the lowest singlet electronic state in VH_3 to have a pyramidal equilibrium structure.

It should be noticed that in all previous theoretical works on ScH_3 and TiH_3, only the ground electronic states of the molecules were examined. But it is known that the question about the ground states in transition metal compounds is far from trivial. In molecules with a three-coordinated transition metal, the situation becomes complicated because of the necessity to take into account the Jahn−Teller effect in low-lying degenerate electronic states. In light of the results of ab initio calculations for first-row transition metal trifluorides,[10−12] one can expect some first-row transition metal trihydrides also to possess low-lying degenerate electronic states at their planar D_{3h} conformations. Our goal was to carry out high-level ab initio calculation of ground and low-lying excited state of the early transition metal trihydrides ScH_3, TiH_3, VH_3, and FeH_3.

2. Computational Methods

Calculations were performed using a local version of the ACES II program package.[13] All-electron calculations were carried out for all molecules. Effective core potential (ECP) calculations were also performed on ScH_3 for comparison. A (14s11p6d1f/10s8p3d1f) basis set on the metal atom and a (6s3p1d/4s2p1d) basis set on the hydrogen atom was used in the all-electron calculations. The metal atom basis sets were Wachters basis[14] modified as in the GAMESS[15] program and augmented with an f function. The f-function exponents on Sc, Ti, and V atoms were taken from ref 16, and that on the Fe atom was obtained from ref 17. The hydrogen basis set was the TZ2P basis set as implemented in ACES II. It is the (5s/3s) Dunning set[18] augmented with two optimized p functions in (2,1) contractions of three primitives. A diffuse s function from ref 19 and a second polarization d function from ref 20 were also added to the TZ2P basis. The effective core potential employed on Sc was as that of Stevens et al.[21] The valence basis set (8s8p6d/4s4p3d)[21] was augmented with an f function. Spherical d and f functions were used in all calculations.

Relative excited-state energies were evaluated with the equation-of-motion coupled cluster method in the singles and doubles approximation (EOM-CCSD).[22] In this method the excited state wave function is generated from a coupled-cluster singles and doubles reference wave function (usually for the ground state) by the action of a wave operator.[22] If the reference state has a closed shell, EOM-CCSD provides a rigorously spin-adapted final state wave function,[22] while when used with a high-spin open-shell reference state the application of EOM-CCSD techniques is limited to only high-spin open-shell excited states[22] (which are nevertheless not spin-adapted). This limitation prevented us from investigating doublet electronic states in FeH_3

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TABLE 1: Equilibrium Internuclear Distances R_e(M−H) (Å), Total Energies E_{min} (au), Harmonic Vibrational Frequencies ω_i (cm^{-1}), and Infrared Intensities A_i (km/mol) in MH_3 (M = Sc, Ti, V, Fe)

MH_3	R_e(M−H)	$E_{min,}$	$\omega_1(A_1')$	$\omega_2(A_2'')$	$\omega_3(E')$	$\omega_4(E')$	A_2	A_3	A_4	method
ScH_3	1.853[c]	−761.452679	1674	340	1570	587	980	1867	372	UHF[a]
	1.850	−47.756783	1677	347	1566	585	974	1863	379	UHF/ECP[b]
	1.838	−761.924660	1658	287	1576	572	913	1592	296	SDQ-MBPT(4)[a]
	1.833	−47.756618	1645	310	1553	564	917	1601	316	SDQ-MBPT(4)/ECP[b]
	1.840	−761.932642	1643	274	1564	570	898	1511	277	CCSD(T)[a]
	1.835	−48.093800	1630	299	1542	562	901	1526	298	CCSD(T)/ECP[b]
TiH_3	1.773	−850.083383	1747	342	1668	588	701	1837	290	UHF[a]
	1.740[d]	−850.592122[d]	1754[d]							CCSD[a]
	1.740	−850.603783	1736	240	1712[e]	633	480	1224	161	CCSD(T)[a]
VH_3	1.713	−944.536417	1814	79	1711	578	798	1852	115	UHF[a]
	1.674[d]	−945.089755[d]	1820[d]							CCSD[a]
	1.675	−945.105111	1795	240	1743	665	524	1127	126	CCSD(T)[a]
FeH_3	1.667	−1264.079484	1883	553	1825	628	494	1162	311	UHF[a]
	1.603	−1264.704955	1882	412	1848	576	403	1225	69	SDQ-MBPT(4)[a]
	1.609	−1264.727733	1831	370	1820[f]	642	358	673	94	CCSD(T)[a]

[a] The calculations are done with M(14s11p6d1f/10s8p3d1f) and H(6s3p1d/4s2p1d) basis sets. [b] (8s8p6d1f/4s4p3d1f) valence basis set on Sc, (6s3p1d/4s2p1d) basis set on H. [c] 2.002 Å with FSGO method[1] and 1.8004 Å with SCF method.[8] [d] These values were computed numerically using polynomial approximation of the energies for grid of four M−H distances. [e] 1580.6 cm^{-1} in Ar matrix IR spectra.[6] [f] 1646.1 cm^{-1} in Ar matrix IR spectra.[7]

TABLE 2: EOM-CCSD Relative Vertical Excitation Energies (cm^{-1}) of Electronic States in MH_3

MH_3	state	all electron	ECP
ScH_3	$X^1A'_1$	0	0
	$(3e')^3(1e'')^1\ a^3A''_2$	30856	31562
	$(3e')^3(5a'_1)^1\ b^3E'$	31164	31773
	$(3e')^3(4e')^1\ A^1E'$	31759	32404
	$(3e')^3(1e'')^1\ c^3E''$	32266	32959
	$(3e')^3(5a'_1)^1\ d^3A'_2$	33880	34321
	$(3e')^3(1e'')^1\ B^1A''_2$	35477	36424
	$(3e')^3(1e'')^1\ C^1E''$	35735	36509
	$(3e')^3(5a'_1)^1\ e^3E'$	36371	36878
	$(3e')^3(1e'')^1\ f^3A''_1$	36644	37501
	$(3e')^1(4e')^1\ D^1A'_2$	36684	37207
	$(3e')^3(1e'')^1\ E^1A''_1$	36731	37574
	$(3e')^3(4e')^1\ g^3A'_1$	39460	40144
	$(3e')^3(4e')^1\ F^1E'$	39777	40400
TiH_3	$(5a'_1)^1\ X^2A'_1$	0	
	$(1e'')^1\ A^2E''$	1516	
	$(4e')^1\ B^2E'$	13175	
VH_3	$(1e'')^2\ X^3A'_2$	0	
	$(1e'')^1(5a'_1)^1\ A^3E''$	1845	
	$(1e'')^1(5a'_1)^1\ a^1E''$	10314	
	$(5a'_1)^2\ b^1A'_1$	10577	
	$(1e'')^1(4e')^1\ B^3A''_2$	13035	
	$(1e'')^1(4e')^1\ C^3A''_1$	13618	
	$(1e'')^1(4\ e')^1\ D^3E''$	16818	
	$(5a'_1)^1(4\ e')^1\ c^1E'$	19439	
FeH_3	$(1e'')^2(5a'_1)^1(4e')^2\ X^6A'_1$	0	
	$(1e'')^4(5a'_1)^1\ a^2A'_1$	16588	
	$(3e')^3(1e'')^3(5a'_1)^1(4e')^2\ A^6A''_2$	18833	
	$(3e')^3(1e'')^2(5a'_1)^2(4e')^2\ B^6E'$	19703	
	$(3e')^3(1e'')^3(5a'_1)^1(4e')^2\ C^6E''$	20508	
	$(1e'')^3(5a'_1)^2\ b^2E''$	21149	
	$(3e')^3(1e'')^3(5a'_1)^1(4e')^2\ D^6A''_1$	21631	
	$(1e'')^3(5a'_1)^2\ c^2A''_1$	22223	
	$(1e'')^3(5a'_1)^2\ d^2A''_2$	22413	
	$(1e'')^4(4e')^1\ e^2E'$	23379	
	$(3e')^3(1e'')^2(5a'_1)^1(4e')^3\ E^6A'_2$	25383	
	$(3e')^3(1e'')^2(5a'_1)^1(4e')^3\ F^6E'$	26978	
	$(3e')^3(1e'')^2(5a'_1)^1(4e')^3\ G^6A'_1$	32731	

molecule, which cannot be well described by high-spin determinant configurations. We could not calculate excitation energies to quartet states in FeH_3 with EOM-CCSD because of the lack of an appropriate single determinant reference CCSD function.

Ground-state molecular parameters are computed at UHF and CCSD(T) levels of theory for all molecules. For ScH_3 and FeH_3, the parameters were also calculated by the SDQ-MBPT(4) method. In the all-electron calculations, equilibrium geometries were optimized using analytical gradients, all vibrational frequencies and infrared intensities in the ground states were calculated using analytical second derivatives of the potential energy surface and analytical first derivatives of the dipole moment.[23] In the ECP calculations equilibrium geometries, vibrational frequencies and IR intensities were calculated numerically using the program VIBMOL described in ref 24.

3. Results and Discussion

Ground States. The calculations showed that all molecules possess a high-spin ground electronic state with the exception of ScH_3, which is a singlet. We found all the molecules to be trigonal planar (D_{3h}). The equilibrium distances M−H, total energies, harmonic vibrational frequencies, and infrared intensities obtained at several level of theory are listed in the Table 1; the results found in the all-electron CCSD(T) calculations are the most reliable. The symmetries and electron configurations of the ground states are presented in Table 2. Some electronic properties such as quadrupole moments, electric field gradients, and the charges on the metal atoms are given in Table 3. Several trends of molecular parameters in the row MH_3 (M = Sc, Ti, V, Fe) can be established: the equilibrium distances R_e(M−H) shorten, stretching frequencies ω_1 and ω_3 increase, and the IR intensities A_3 and A_4 decrease.

Excited States. The vertical excitation energies to several electronic states of the MH_3 molecules at their D_{3h} conformations are listed in Table 2. The energies were calculated at the M−H distances which had been optimized for the ground-state D_{3h} structures at the CCSD(T) level of theory. Relative energies of both singlet and triplet excited states in ScH_3, doublet states in TiH_3, triplet excited states in VH_3 and the sextet excited state in FeH_3 were found by EOM-CCSD calculations using the ground-state wave functions as references. The $b^1A'_1$ state was taken as the reference state in EOM-CCSD calculations of singlet states in VH_3. The relative energy of this state listed in Table 2 was found directly by the CCSD(T) method. For the other singlet states in VH_3 the EOM-CCSD energies were added to the computed relative energy for the $b^1A'_1$ state. A similar procedure was applied for doublet electronic states in FeH_3. The $a^2A'_1$ state was assigned as the reference in EOM-CCSD calculations of doublet states. The energy of the $a^2A'_1$ state was

TABLE 3: CCSD(T) Quadrupole Moments Θ_{zz}, Electric Field Gradients q, and Charge on the Metal Atom for Transition Metal Trihydrides MH_3 (M = Sc, Ti, V, Fe)[a]

MH_3	Θ_{zz}	q_{zz}(M)	q_{xx}(H)	q_{yy}(H)	charge(M)
ScH_3	9.579	1.895	0.064	−0.032	0.530
TiH_3	5.350	1.321	0.073	−0.035	0.633
VH_3	5.937	1.125	0.084	−0.036	0.702
FeH_3	5.092	3.801	0.095	−0.051	0.708

[a] All values in atomic units.

found using the so-called QRHF−CCSD method.[25] The CCSD wave function of the $a^2A'_1$ state was formed from closed-shell RHF wave function for FeH_3^- ion.[26] The electron configurations that made the largest contribution to the excited states wave functions are also indicated in Table 2. The results show that the first excited states of ScH_3 and FeH_3 lie quite high with respect to their ground states while the molecules TiH_3 and VH_3 have low-lying degenerate electronic states.

Correlation Effects. Comparison of the CCSD(T) and UHF results proves the importance of accurate accounting for electron correlation in order to determine molecular parameters in MH_3 molecules. The correlation corrections to M−H internuclear distances in MH_3 molecule turned out to be significant, from 0.013 Å in ScH_3 to 0.058 Å in FeH_3. Judging by the CCSD results for TiH_3 and VH_3 presented in Table 1, the contributions of triple excitations in the correlation effects for M−H bond lengths are not substantial. For organic and many other compounds, addition of electron correlation to Hartree−Fock basis set normally causes bonds to lengthen. This effect is generally attributed to the admixture of antibonding orbitals, which weaken the bond. However, it is known that the effect is more complex in calculation of transition metal compounds. For ScF_3, correlation causes an increase in bond length M−F,[27,11] while for other first-row transition metal trifluorides it causes a decrease.[11] However, the present calculations show that the effect of correlation is to shorten the internuclear distance in all of the trihydrides studied.

Despite the significant shortening of M−H distances due to the correlation effects, the values of the stretching vibrational frequencies ω_1 and ω_3 change only slightly. The values of the totally symmetric frequencies ω_1 increase with the CCSD method (see result for TiH_3 and VH_3 in Table 1) and decrease at the CCSD(T) level of theory while the bond lengths M−H shorten. The correlation corrections for ω_2 out-of-plane vibration frequencies in MH_3 are more significant. Infrared intensities of MH_3 also turned out to be strongly influenced by accounting for electron correlation. The largest correlation corrections were found for the infrared intensities A_3 and A_4 in FeH_3; the CCSD(T) values decrease by 2−3 times compared to the UHF results.

SDQ-MBPT(4) and ECP Calculations. In the point of view of computational techniques it is interesting to consider the results of the calculations with the SDQ-MBPT(4) method and the calculation with use of effective core potentials. The SDQ-MBPT(4) method is less time-consuming than the CCSD(T) one and the effective core potential technique decreases the requirements on computer resources compare to all-electron calculations. The results of calculations of all parameters for closed-shell ScH_3 with the SDQ-MBPT(4) method are close to the CCSD(T) results (Table 1). Nearly all of the correlation corrections to molecular parameters have the same sign as the corresponding values found with CCSD(T), but most of them are smaller. However, for FeH_3 the SDQ-MBPT(4) method leads to values of frequency ω_4 and infrared intensity A_3 which differ significantly from results obtained with the CCSD(T) method.

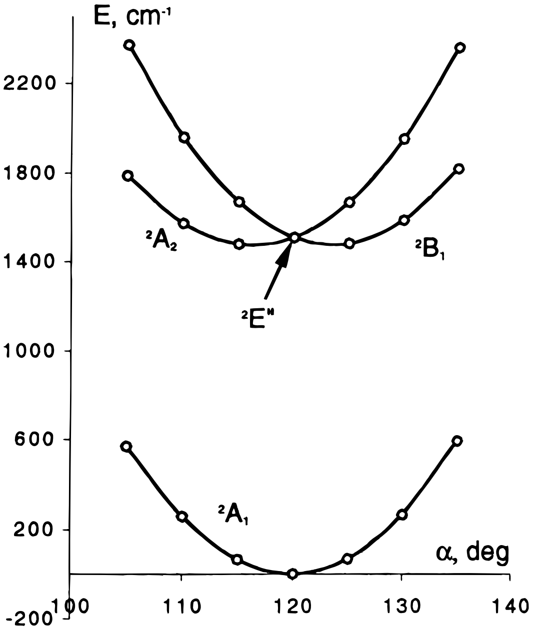

Figure 1. TiH_3 C_{2v} energy as a function of bond angle α($H_{(2)}$−Ti−$H_{(3)}$).

ECP calculations predict the same sequence of excited states in ScH_3 with the exception of the $f^3A''_1$ and $D^1A'_2$ states. Relative energies obtained with ECP are 500−900 cm^{-1} more than the all-electron values. The differences between all-electron and ECP values of the ground-state parameters are not so large, 0.003−0.005 Å for internuclear distance in Sc−H, 2−25 cm^{-1} for vibrational frequencies, and 2−21 km/mol for infrared intensities. It should be noticed though that the differences between all-electron and ECP values, which are found by the SDQ-MBPT(4) and CCSD(T) methods are larger than for the UHF method.

ScH_3. The conclusion about a D_{3h} equilibrium structure of ScH_3 is in agreement with results of the previous calculations,[1,8] but the Sc−H distance found in this work differs significantly from the value found previously.[1,8] Several excited states of ScH_3 lie 30000 cm^{-1} above the ground state and are located very close to each other. These excited states result from excitation of an electron from the $3e'(p_x(Sc)-s(H),p_y(Sc)-s(H))$ orbital to either the $1e''(d_{xz},d_{yz})$ or the $5a'_1(d_{3z^2-r^2})$ or the $4e'(d_{x^2-y^2},d_{xy})$ one. The lowest excited electronic state in ScH_3 cannot be determined unambiguously using only the result of single-point calculations of vertical excitation energy. It may be either the $a^3A''_2$ or the b^3E' triplet state because the difference between them is only 308 cm^{-1}. The Jahn−Teller effect[28,29] could further decrease the b^3E' state energy sufficiently to move it below the $a^3A''_2$ state. To our knowledge, there are no available experimental data on the structure and spectra of scandium trihydride.

TiH_3. Results of our UHF calculations of the ground-state equilibrium Ti−H distance, vibrational frequencies, and IR intensities for TiH_3 (Table 1) are close to those reported in ref 6. The differences in the magnitudes can be explained by differences in the basis sets used in the two studies.

At the EOM-CCSD level of theory, the relative energy of the lowest electronic state $^2E''$ in TiH_3 is only 1516 cm^{-1}. Therefore, the possibility that the Jahn−Teller effect[28,29] could lower the energy of $^2E''$ state enough to make it the ground state was investigated. Figure 1 presents the scans of surfaces of the low-lying TiH_3 electronic states $^2A_1$, $^2A_2$, and $^2B_1$ along the coordinate which corresponds to the valence angle α($H_{(2)}$−

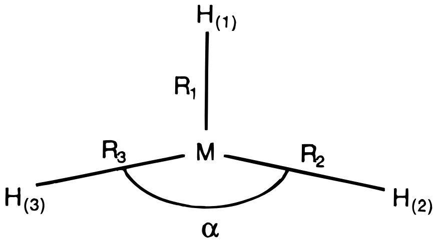

Figure 2. Internal coordinate notation for MH_3 of C_{2v} symmetry.

TABLE 4: C_{2v} Symmetry Equilibrium Geometries and Jahn−Teller Stabilization Energies ΔE_{JT} of TiH_3 Calculated by EOM-CCSD Theory

	$^2A_2$	$^2B_1$
$R_1(Ti-H_{(1)})$, Å	1.754	1.733
$R_2(Ti\text{-}H_{(2)})=R_3(Ti-H_{(3)})$, Å	1.741	1.747
$\alpha(H_{(2)}-Ti-H_{(3)})$, deg	116.2	123.7
ΔE_{JT}, cm^{-1}	39	37

$Ti-H_{(3)}$) (Figure 2). Electronic states $^2A_2$ and $^2B_1$ arise from electronic state $^2E''$ with deformation of molecular structure from D_{3h} to C_{2v} symmetry. The scans were calculated under the assumption that all M−H distances in TiH_3 are constant and equal to 1.745 Å which corresponds to the equilibrium M−H distance for the $^2E''$ electronic state (D_{3h} conformation) at the EOM-CCSD level. According to these calculations, the $^2A_2$ electronic state minimum corresponds to $\alpha(H_{(2)}-Ti-H_{(3)}) = 116.3°$ and lies 35 cm^{-1} below the $^2E''$ state energy (Figure 1). The minimum of the $^2B_1$ electronic state is located at $\alpha(H_{(2)}-Ti-H_{(3)}) = 123.5°$ and lies 33 cm^{-1} below the $^2E''$ state energy. The results of full C_{2v} optimization for $^2A_2$ and $^2B_1$ electronic states performed analytically are listed in Table 4. Thus, the Jahn-Teller distortion of $^2E''$ electronic state geometry in TiH_3 is not large, up to 0.01 Å for internuclear distances Ti−H and less than 4° for the H−Ti−H valence angle. The magnitude of the Jahn-Teller stabilization energy in the first excited electronic state $^2E''$ (39 cm^{-1}) is small compare to the relative energy of the $^2E''$ electronic state (1516 cm^{-1}). Therefore, the Jahn−Teller effect cannot change the conclusion in regard to the ground electronic state of TiH_3.

Only one band located at 1580.6 cm^{-1} in the IR spectra of the Ti + H_2 system in an Ar matrix was reported to belong to TiH_3.[6] This band was assigned to the degenerate ν_3 vibration. Indeed, according to ab initio calculations, degenerate M−H stretching vibrations in MH_3 molecules have the highest IR intensities, but the theoretical ω_3 frequency found at the CCSD(T) level of theory is 131 cm^{-1} higher than the experimentally assigned fundamental stretch.[6] Perhaps the direct comparison of calculated harmonic frequency ω_3 and the observed band ν_3 in the IR spectra[6] for TiH_3 is inappropriate. The low-lying degenerate electronic state in TiH_3 molecule has the relative energy 1516 cm^{-1} which is less than theoretical stretching harmonic frequencies $\omega_1 = 1736$ cm^{-1} and $\omega_3 = 1712$ cm^{-1}. Therefore, a higher theoretical level that takes into account the vibronic coupling of the ground and first excited state should be applied for complete description of the low-lying energy levels in TiH_3.

VH_3. The ground state of VH_3 is a triplet $^3A'_2$. The first excited state is a triplet $^3E''$, and it is located only 1845 cm^{-1} higher than the ground state $^3A'_2$. Scans of the ground $^3A_2$ and two excited $^3A_2$ and $^3B_1$ electronic states of VH_3 which arise with $D_{3h} \rightarrow C_{2v}$ deformation of the molecule were calculated in the same way as for TiH_3. At the EOM-CCSD level the equilibrium V−H distance of D_{3h} conformation in the $^3E''$ state is equal to 1.674 Å. The calculations show that Jahn-Teller effect in the $^3E''$ electronic state of VH_3 is very small; the minimum in the $^3A_2$ electronic state corresponds to an $\alpha(H_{(2)}-Ti-H_{(3)})$ valence angle of 121.6°, the minimum of $^3B_1$ corresponds to $\alpha(H_{(2)}-Ti-H_{(3)}) = 118.6°$, and both these minima lie only 5 cm^{-1} below the $^3E''$ state energy.

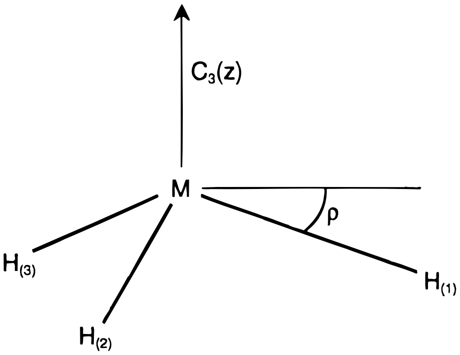

Figure 3. Out-of-plane internal coordinate ρ for MH_3.

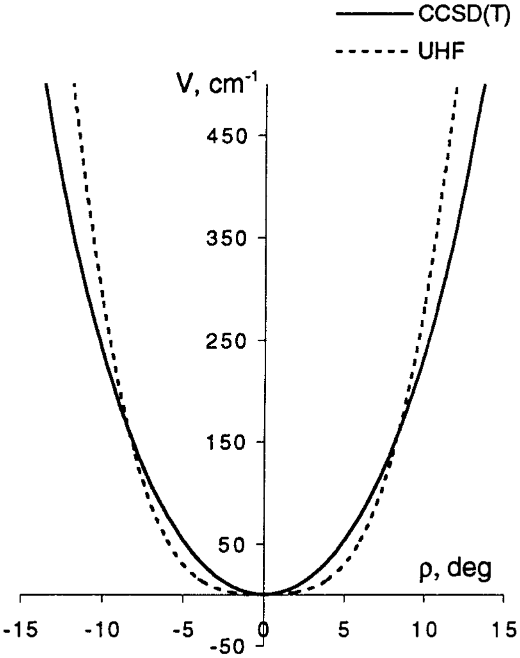

Figure 4. Out-of-plane potential function of VH_3 calculated at UHF and CCSD(T) levels of theory.

According to our calculations, the singlet state $^1A'_1$ of VH_3 that apparently was studied in ref 1 lies 10577 cm^{-1} above the ground state $^3A'_2$ at the D_{3h} conformation. The previous authors apparently did not look for triplet states. However, this is not even the lowest singlet state in VH_3; the $^1E''$ state lies 263 cm^{-1} lower than $^1A'_1$.

The harmonic nonplanar frequency ω_2 in VH_3 calculated analytically with UHF method is only 79 cm^{-1}. The corresponding CCSD(T) value is 240 cm^{-1}. To explore further the large difference (a factor of 3) between these two values, we undertook additional calculations of the out-of-plane potential in VH_3. At both UHF and CCSD(T) levels of theory, the energies of C_{3v} structures of VH_3 at several values of the coordinate ρ were found. The coordinate ρ corresponds to the angle between the M−H bond and the perpendicular to the C_3(*z*) symmetry axis of the molecule (see Figure 3). V−H bond lengths were fixed to the equilibrium V−H values of the D_{3h} structure. A polynomial approximation of the C_{3v} energies

(Figure 4) showed that the nonplanar potentials of VH_3 found with the two methods have different shapes; the UHF potential function is mostly quartic, while the CCSD(T) one is almost harmonic. We of course consider the latter more reliable.

The ESR and IR spectra of the V+ H_2 system in Ar matrix were investigated by Van Zee et al.,[30] but no specific data on a VH_3 molecule were reported.

FeH_3. For FeH_3 molecule, the excited state $^2A'_2$ listed in Table 2 may not be the lowest one. A quartet electronic state is most likely to be the first excited electronic state as in FeF_3 molecule.[11] A band located at 1646.1 cm^{-1} in the IR spectra of Fe + H_2 in an Ar matrix was assigned to ν_3 vibration of FeH_3.[7] The ω_3 harmonic frequency of free FeH_3 molecule calculated at CCSD(T) level is 1820 cm^{-1}. Possible sources of the large difference between the theoretical ω_3 and experimental ν_3 frequency values in FeH_3 are the neglect of the anharmonicity of the vibrations and the effect of the influence of the Ar matrix on the structure and vibrational spectrum of the FeH_3 molecule.

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