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First principles study of cobalt hydride, CoH, and its ions CoH⁺ and CoH⁻

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The electronic structure of the diatomic species CoH, CoH⁺, and CoH⁻ have been studied mainly by multireference configuration interaction (MRCI) methods and basis sets of quintuple quality. The restricted coupled-cluster with iterative singles + doubles + quasi-perturbative connected triples, RCCSD(T), approach was also employed, limited however to the ground states only. At the MRCI level we have constructed 27 (CoH), 24 (CoH⁺), and 12 (CoH⁻) potential energy curves correlating adiabatically to six, seven, and two energy channels, respectively. For the ground states scalar relativistic and core-subvalence effects have been taken into account. We report energetics, spectroscopic parameters, dipole moments, excitation energies, and spin-orbit coupling constants. Our CoH calculated results are in accord with experiment, but there is an interesting discrepancy between theory and experiment concerning the dipole moment, the former being significantly larger than the latter. Experimental results on CoH⁺ and CoH⁻ are scarce. The ground state of CoH, CoH⁺, and CoH⁻ are definitely of ³Φ, ⁴Φ, and ⁴Φ symmetries with calculated (experimental) dissociation energies $D_0^0 = 46.4 \pm 0.5(45.0 \pm 1.2)$, $49.6(47 \pm 2)$, and $45.6(43.1 \pm 1.2)$ kcal/mol, respectively. In all 24 calculated CoH states, a Co-to-H charge transfer of 0.2–0.3 e⁻ is recorded; in CoH⁻, however, the negative charge resides almost exclusively on the Co atom. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4734595>]

I. INTRODUCTION

The present work is a comprehensive high level *ab initio* study of the diatomic cobalt hydride, CoH, and its ions CoH⁺ and CoH⁻. The simplicity of the hydrogen atom makes the theoretical study of diatomic hydrides (ZH) relatively easier and more accurate as compared to corresponding non-hydride systems. Hence *ab initio* studies of the ZH diatomics are of importance for reasons of benchmarking and validation of our methods and techniques, as well as to test new ones towards a better understanding of the correlation problem. Therefore, in general, one would expect the existence of a large body of accurate *ab initio* studies on the ZH class of molecules. Though this is the case for the elements of the second (Z = Li–F) and third (Z = Na–Cl) row of the Periodic Table, it is not so for the 3d-transition metal hydrides MH, M = Sc–Cu. In particular, all electron first principles calculations on CoH are very few indeed (*vide infra*). There is, however, a considerable number of experimental publications on CoH (Refs. 1–21) beginning in 1937 by the work of Heimer,¹ who through emission spectroscopy observed a $22\,243\text{ cm}^{-1} \Omega' = 4 \rightarrow \Omega'' = 4$ transition, correctly predicting the symmetry of these two states as ³Φ₄. The ground state of CoH (³Φ) was determined in 1981 by Klynning and Kronekvist² by rotational spectroscopy, and conclusively confirmed a few years later by Beaton *et al.*⁹ by laser magnetic resonance (LMR) spectroscopy. Table I collects the majority of experimental results on CoH. The dipole moment of two states have been also measured recently by Steimle's group,²¹ $\mu = 1.88 \pm 0.08$ (X³Φ₄) and 0.01 ± 0.08

D (A'³Φ₄); the A' state is located $\sim 12\,500\text{ cm}^{-1}$ above the X state; see Table I.

Theoretical *ab initio* work on CoH is confined to four publications,^{22–24,26} the first one by Das²² who studied the entire 3d–MH (M = Sc–Cu) sequence by MCSCF–pseudopotential methods. In 1986 Chong *et al.*²³ examined the ground states of the 3d–MH hydrides (M = Sc–Zn) by the modified coupled pair functional (MCPF) approach and better than double-zeta (DZ) basis sets. The first attempt for a more systematic theoretical investigation of CoH is that of Freindorf *et al.*²⁴ These workers studied 34 states of CoH around equilibrium (12 singlets, 16 triplets, and 6 quintets), through the MRD–CI multireference configuration interaction approach of Buenker and Peyerimhoff.²⁵ They report bond distances (r_e), energy separations (T), and harmonic frequencies (ω_e). Their calculations, however, suffer from rather small basis sets and limited CI expansions.²⁴ The most recent first principles work on CoH is that of Hirano and co-workers²⁶ published in 2007. Employing MRCI+Q(+Q = Davidson correction) and MRCPA methods combined with large Slater-type basis sets (9s7p3d2f1g/C₀5s3p1d/H), they calculated around equilibrium the X³Φ and ⁵Φ states of CoH; their main target was the accurate determination of the bond distance of the X³Φ state. They report r_e , ω_e , T_e (⁵Φ–X³Φ) and the dipole moment of the X³Φ state, $\mu = 3.23\text{ D}$.²⁶ Finally, between 1997 and 2008, six density functional theory (DFT) calculations have appeared in the literature using a variety of functionals,^{27–32} focusing exclusively on the ground states of CoH and related diatomics. As is usually the case, at least for molecules containing 3d-transition metals, DFT results are a function of the functionals used.

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TABLE I. Experimental data of CoH. Dissociation energies D_0 (kcal mol⁻¹), bond distances, r_e (Å), harmonic frequencies, ω_e (cm⁻¹), and energy separations T (cm⁻¹).

State ^a	D_0	r_e	ω_e	T
(X) ³ Φ_4 ^b		1.542 (=r ₀)	1890.0 ($\Delta G_{1/2}$)	0.0
A ³ Φ_4 ^b				~22 240
(X) ³ Φ_4 ^c		1.529 (=r ₀)		0.0
A ³ Φ_4 ^c		1.614 (=r ₀)		~22 240
(X) ³ Φ ^d			1655	
X ^e	45.1 ± 3			
X ^f	39 ± 6			
X ^g	42.2 ± 3			
(X) ³ Φ ^h	54 ± 10			
(X) ⁴ Φ_4 ⁱ		1.542	1925.2	0.0
(⁵ Φ) ⁱ		1.67 ± 0.05		6625 ± 110
X ^j	46 ± 3			
X ³ Φ_4 ^k		1.544 (=r ₀)		0.0
(³ Δ_3) ^k				2469 ± 3
X ^l	46 ± 3			
³ Φ_4 ^m		1.5171	1926.7	
X ⁿ	46.6 ± 3.2			
X ³ Φ ^o		1.514		
X ³ Φ_4 ^p		1.526 (=r ₀)		0.0
A ³ Φ_4 ^p		1.750 (=r ₀)		~12 360
(³ Δ) ₃ ^p				~2469
X ^q	45.0 ± 1.2			
X ³ Φ_4 ^r		1.5313	1858.79 ($\Delta G_{1/2}$)	
A ³ Φ_3 ^r				~12 000
X ³ Φ_4 ^s		1.533		
X ³ Φ_3 ^s		1.518		
A ³ Φ_4 ^s				12 358.4
A ³ Φ_3 ^s		1.6352 (=r ₀)		12 645.0
A ³ Φ_4 ^s		1.615 (=r ₀)		22 243.2

^aAssignments in parentheses show uncertainty.

^bReference 1; emission spectroscopy; r₀ from B₀ = 7.151 cm⁻¹.

^cReference 2; rotational analysis; r₀(X³ Φ_4) from B₀ = 7.279 cm⁻¹.

^dReference 3; absorption spectroscopy; also $\omega_e x_e = 63$ cm⁻¹.

^eReference 4.

^fReference 5; thermochemical reactions of Co⁺ with H and alkanes.

^gReference 6; fourier transform mass spectrometry.

^hReference 7; ion beam techniques.

ⁱReference 8; photoelectron spectroscopy; also $\omega_e x_e(X^3\Phi) = 34.6$ cm⁻¹.

^jReference 10; ion beam mass spectrometry.

^kReference 11; rotational spectroscopy. Also for the ground state A_{SO} = -242.7 ± 1 cm⁻¹.

^lReference 12; ion beam mass spectrometry.

^mReference 13; CO-Faraday laser magnetic resonance spectroscopy; r_e obtained from B_e = 7.391 53(7) cm⁻¹. Also $\omega_e x_e = 34.6$ cm⁻¹ and $\alpha_e = 0.219$ 74(2) cm⁻¹.

ⁿReference 14; ion beam mass spectrometry.

^oReference 16; far infrared LMR spectroscopy.

^pReference 17; laser induced fluorescence spectroscopy.

^qReference 18; ion beam thermochemistry.

^rReference 19; Fourier transform emission spectroscopy; r_e obtained from B_{e,Ω=4} = 7.149 160(57) cm⁻¹ and $\alpha_e = 0.212$ 444(93) cm⁻¹.

^sReference 20; near infrared emission spectroscopy; also A_{SO} = -242.3 cm⁻¹.

Concerning now the cation CoH⁺, the only experimental parameter known is the dissociation energy, $D_0^0 = 47 \pm 2$ kcal/mol, determined through ion beam mass spectrometry by the Armentrout group.^{10,33} A more recent, but apparently less accurate value given also by the same group is, $D_0^0 = 42 \pm 4$ kcal/mol.¹⁴ Using the first D_0^0 number along with the experimental dissociation energy of CoH,¹⁸ we can (indirectly) determine an experimental ionization energy (IE) of CoH through the energy conservation expression, IE(CoH)

$$= D_0(\text{CoH}) - D_0(\text{CoH}^+) + \text{IE}(\text{Co}), \text{ or } \text{IE}(\text{CoH}) = (45.0 \pm 1.2 - 47 \pm 2) \text{ kcal/mol} + 7.864 \text{ eV} = 7.8 \pm 0.1 \text{ eV}.$$

We have traced six *ab initio* publications on CoH⁺, the first by Schilling *et al.*^{34(a)} who correctly predicted the ground state of CoH⁺ as ⁴ Φ . These workers studied the ground^{34(a)} and one-to-four low-lying excited states^{34(b)} of the MH⁺ (M = Sc–Zn) cations by the generalized valence bond + singles + doubles CI method (GVB+1+2/DZ+P). See also Ref. 34(c). In 1987 Pettersson *et al.*³⁵ examined the ground states of the 3d–MH⁺ (M = Sc–Cu) and 4d–MH⁺ (M = Y–Ag) species through the MCPF/[8s6p4d3f/c₀4s3p/h] methodology, including scalar relativistic effects by first order perturbation theory. The first systematic *ab initio* work on CoH⁺ is that of Anglada *et al.*³⁶ These authors constructed MRD–CI/[8s6p3d1f/c₀2s1p1d/h] (Ref. 25) limited potential energy curves (PEC) from r = 2.0 to 5.0 bohr for 20 states, reporting numerical results (r_e, D_e, ω_e , $\omega_e x_e$, and α_e) for 15 states, 8 quartets, and 7 doublets. The total energy of the X⁴ Φ state at the MRD–CI+Q level is: E = -1381.7018 E_h.³⁶ Their results, particularly for the lowest states, compare favorably with the present ones, although our total MRCI+Q energy of the X⁴ Φ state is by 298 mE_h lower (see Table IV). Ten years later Shaik and co-workers³⁷ studied the ground states of the 3d–MH⁺ (M = Sc–Zn) series by the valence–bond method (VB–SCF), aiming at the interpretation of their bonding character within the spirit of the VB theory. Finally, Nakao *et al.*³⁸ in a study of the water activation by Co⁺, they also examined the CoH⁺ cation through MRCI+Q calculations coupled with Stuttgart relativistic small core (1s²2s²2p⁶) effective potentials augmented by a [6s5p3d1f/c₀aug–cc–pVTZ/h] valence basis set. At this level they report r_e, D_e, and ω_e values for four quartets, that is, X⁴ Φ , ⁴ Σ^- , ⁴ Π , and ⁴ Δ . Their findings will be compared with ours later on. It should be mentioned also that between 1994 and 2008, six DFT studies on the ground state of CoH⁺ appeared in the literature (Refs. 27, 29, 32, and 39–41).

We now turn to the anion CoH⁻. From the only one experimental work by photoelectron spectroscopy of Miller *et al.*,⁸ we know the following parameters of CoH⁻: r₀ = 1.67 ± 0.03 Å, $\omega_e = 1300 \pm 150$ cm⁻¹, and the EA(electron affinity) of CoH, EA = 0.671 ± 0.010 eV; they also assigned tentatively the ground state of CoH⁻ to ⁴ Φ .⁸ Using the experimental EAs of CoH and H,⁴² an experimental dissociation energy of CoH⁻ can be deduced: $D_0(\text{CoH}^-) = D_0(\text{CoH}) + \text{EA}(\text{CoH}) - \text{EA}(\text{H})$, or $D_0(\text{CoH}^-) = (45.0 \pm 1.2) \text{ kcal/mol} + (0.671 \pm 0.010 - 0.7542) \text{ eV} = 43.1 \pm 1.2 \text{ kcal/mol}$.

Through the MRD–CI method (Ref. 25), Freindorf *et al.*²⁴ determined four stable states of CoH⁻, that is, X⁴ Φ , ⁴ Π , ⁴ Σ^- , and ² Φ . Apart from their stability with respect to the X³ Φ state of CoH, no other information is given in Ref. 24.

The above exposition of the experimental and theoretical work on CoH and CoH[±] shows the need for a fresh, systematic, and high level theoretical study of the electronic structure of these species. Thus we have performed large scale variational multireference calculations for 27, 24, and 12 states of CoH, CoH⁺, and CoH⁻, respectively; for the ground states of CoH and CoH[±] we have also performed single reference coupled-cluster calculations. We report PEC, total

equilibrium energies, spectroscopic parameters, dipole moments, Mulliken charges, and spin–orbit coupling constants.

The paper is structured as follows: Section II refers to technical aspects, Secs. III A, III B, and III C pertain to results and discussion on CoH, CoH⁺, and CoH[−], respectively, while the final Sec. IV gives a short overview and evaluation of our findings.

II. COMPUTATIONAL DETAILS

For the Co atom the correlation consistent (cc)⁴³ basis set of quintuple cardinality of Balabanov and Peterson⁴⁴ was employed, combined with the cc-pV5Z basis set of H,^{43,45} generally contracted to [9s8p6d4f3g2h1i/c₀5s4p3d2f1g/H] ≡ 5ζ. The 5ζ basis was used for the calculation of CoH and CoH⁺, whereas for the CoH[−] it was augmented by a series of diffuse functions for both atoms contracted to [10s9p7d5f4g3h2i/c₀6s5p4d3f2g/H] ≡ A5ζ. The augmentation for both Co and H was deemed as necessary due to the similarity of the electron affinities of H (Ref. 42) and Co,⁴⁶ EA = 0.7542 and 0.662 ± 0.01 eV respectively. For estimating the core–subvalence effects (3s²3p⁶), a set of weighted core functions⁴⁴ were grafted to the 5ζ basis set resulting to a contracted set [11s10p8d5f4g3h2i/c₀5s4p3d2f1g/H] ≡ C5ζ of order 266. All PECs were constructed by the complete active self consistent field (CASSCF) + single + double replacements method (CASSCF +1 +2 = MRCI) under C_{2v} symmetry restrictions. The reference spaces are defined by allotting 10 electrons to 10 orbitals (3d4s4p/c₀ + 1s/H) for CoH, 9 e[−] to 7 orbitals (3d4s/c₀ + 1s/H) for CoH⁺, and 11 e[−] to 13 orbitals (3d4s4p/c₀ + 1s2s2p_{x,y}/H) for CoH[−]. The corresponding core reference spaces are defined by allotting 18 electrons to 14 orbitals (3s3p3d4s4p/c₀ + 1s_H) for CoH, and 17 electrons to 11 orbitals (3s3p3d4s/c₀ + 1s/H) for CoH⁺. To make the core calculations feasible, however, no more than two electrons were excited to the extra three 4p orbitals. Internally contracted (ic)⁴⁷ valence MRCI wave functions were calculated by single + double excitations out of the reference spaces. For the ground states of CoH and CoH⁺, core correlation effects were taken into account by including the 3s²3p⁶ electrons in the CI procedure (C–MRCI). The icMRCI (MRCI) expansions for the X³Φ and X⁴Φ states of CoH and CoH⁺ contain 2.2 × 10⁶ (1.5 × 10⁸) and 2.6 × 10⁵ (6.9 × 10⁶) configuration functions (CF), respectively. Corresponding CF numbers for the icC–MRCI (C–MRCI) calculations are 4.7 × 10⁷ (3.2 × 10⁹) and 1.6 × 10⁶ (1.2 × 10⁸). CI calculations for the CoH[−] anion, including the subvalence 3s²3p⁶ electrons, proved to be beyond our computing capacities due to very large icMRCI expansions. For the X³Φ state of CoH we performed larger MRCI calculations (MRCI–L) by including the five 4d functions of Co in the reference space. To make the MRCI–L computations feasible we were forced to limit the excitations to the 4p + 4d space to singles and doubles; the icMRCI–L expansions are ~2.6 × 10⁷ CFs long.

For the ground states of CoH and CoH[±], restricted coupled-cluster with iterative singles + doubles + quasi-perturbative connected triples (RCCSD(T))⁴⁸ calculations have been also performed. The states examined are of open-shell character with leading equilibrium coefficients close to

~0.6–0.7, i.e., not of the single reference type (C₀ > 0.8–0.9). For such systems we are forced to use natural CASSCF orbitals, because HF orbital based calculations do not converge. Scalar relativistic effects for the ground states of CoH and CoH[±] have been taken into account through the second order Douglas–Kroll–Hess (DKH2) approach,^{49,50} using the corresponding relativistic basis sets provided by Balabanov and Peterson.⁴⁴ Spin–orbit (SO) coupling constants (A) are calculated by diagonalizing the $\hat{H}_e + \hat{H}_{SO}$ Hamiltonian within the \hat{H}_e MRCI eigenvectors, where \hat{H}_{SO} is the full Breit–Pauli operator. Basis set superposition errors (BSSE) estimated by the standard counterpoise method⁵¹ are no more than 0.20 kcal/mol. Spectroscopic parameters have been determined by solving numerically the one dimensional Schrödinger equation. One electron basis sets have resulted from state average CASSCF calculations. This way symmetry adaptation, i.e., correct |Λ| symmetry, is achieved and a balanced configuration mixing of states of the same symmetry is taken into account.

Perhaps a word should be said at this point as to the size extensivity and size-consistency terms, the former referring to linear scaling and the latter to energy additivity of non-interacting fragments. Certainly the MRCI calculations are size-nonextensive, therefore our equilibrium parameters have been corrected by the Davidson (+Q) correction.⁵² The most conspicuous property that requires the energy calculation at “infinite” distance between the fragments (non-interacting limit), is the binding energy. It turns out that our MRCI calculations are size-consistent, that is, the separate energy sum E(Co) + E(H) or E(Co⁺) + E(H), is equal to the total energy of the supermolecule at internuclear distances of 30.0 bohr; the same is practically true for the CoH[−] anion. This is expected in the present case because one of the fragments is a one- or two electron (H or H[−]) system. Certainly the +Q correction is indispensable for correctly describing the electronic states. However the question is whether or not this correction is needed when the size–consistency is zero (CoH^{0,±}). It has nothing to correct upon at 30 bohr. With no quadruple excitations from the H(H[−]) atom at this distance, the calculation of the D_e value at the MRCI+Q level results in abnormally high values. Therefore we do not endorse the +Q correction for the D_e value especially.

All calculations have been performed by the MOLPRO2006 code.⁵³

III. RESULTS AND DISCUSSION

A. CoH

The ground state of Co atom is $a^4F(4s^23d^7)$ with the first six excited states $b^4F(4s^13d^8)$, $a^2F(4s^13d^8)$, $a^4P(4s^23d^7)$, $b^4P(4s^13d^8)$, $a^2D(4s^13d^8)$, and $a^2G(4s^23d^7)$, 0.417, 0.878, 1.634, 1.830, 1.967, and 1.986 eV higher (M_J averaged), respectively.⁵⁴ Strongly attractive (non-van der Waals) interactions of Co + H(2S) can only be traced to a 4s¹3d⁸ configuration of the Co atom whereas 4s²3d⁷ configurations lead to repulsive interactions. Consequently, relatively strongly bound states correlating adiabatically to 4s²3d⁷ distributions are the result of avoided crossings or interactions with states

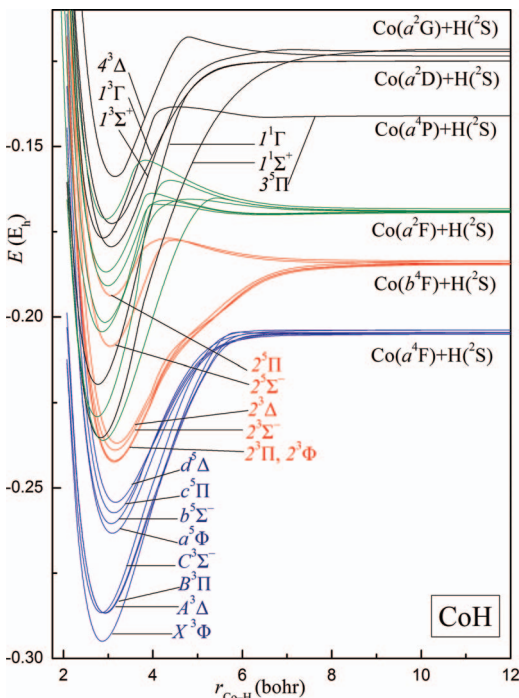


FIG. 1. MRCI+Q/5 ζ PECs of 27 states of CoH. In ascending energy order the states of the third (green) channel are: $1^1\Pi$, $1^1\Delta$, $1^1\Phi$, $3^3\Delta$, $3^3\Phi$, $3^3\Pi$, and $1^1\Sigma^-$.

of the same symmetry emanating from higher $4s^1 3d^8$ configurations (see Fig. 1). The interaction of Co (a^4F , b^4F) + $H(^2S)$ gives rise to $8(a^4F) + 8(b^4F) = 16^{2S+1}\Lambda$ molecular states, triplets and quintets, of Σ^- , Π , Δ , and Φ angular momentum, whereas from the third channel, $Co(a^2F) + H(^2S)$, we get singlets and triplets. We have calculated all 16 PECs related to the first two channels (states $^5\Delta$ and $^5\Phi$ are repulsive), all but the $^3\Sigma^-$ state out of the third channel, one out of four from the $Co(a^4P) + H(^2S)$ fourth channel, none from the $Co(b^4P)$ end fragment, and $3 + 2$ states from the channels $Co(a^2D$, a^2G) + $H(^2S)$, a total of 27 adiabatically bound states covering an energy range of 3.60 eV. Atomic energy separations of $Co(b^4F$, a^2F , a^4P , a^2D , a^2G) – $Co(a^4F)$ obtained at the supermolecule MRCI+Q/5 ζ level are (experimental results in parentheses) 0.55(0.417), 0.94(0.878), 1.71(1.634), 2.15(1.986), and 2.22(1.967) eV respectively. The agreement between theory and experiment can be considered as quite good.

1. $X^3\Phi$

Numerical results for the $X^3\Phi$ state of CoH are given in Table II, including experimental and selected theoretical values from the literature for easy comparison; Fig. 1 displays MRCI+Q/5 ζ PECs. Observe that core ($3s^2 3p^6$) + relativistic effects combined, reduce the bond distance (δr_e) and binding energy (δD_e) by 0.017 Å and 6.2 kcal/mol at the MRCI level; corresponding numbers at the coupled-cluster level are 0.023 Å and 2.8 kcal/mol. For core effects alone $\delta r_e \sim 0.0$ Å in both methods, but $\delta D_e = -1.8$ (MRCI) and $+1.5$ (RCCSD(T)) kcal/mol. At the highest level of theory C–MRCI+DKH2 (C–RCCSD(T)+DKH2) [MRCI–L+DKH2 + core correction], we obtain $D_0^0 = 43.7$ (45.9) [48.7–1.8 = 46.9] kcal/mol with respect to the ground state atoms. Considering the last

two numbers as more accurate, the recommended calculated dissociation energy of CoH is $D_0^0 = 46.4 \pm 0.5$ kcal/mol, as compared to an experimental value of 45.0 ± 1.2 kcal/mol.¹⁸

We discuss now the bond distance, r_e . In 1994 Beaton *et al.*¹⁶ from their measured rotational constant, B_0 , and the vibration–rotation interaction constant $\alpha_e = 0.219\,74(2)$ cm^{-1} of Lipus *et al.*,¹³ they obtained $r_e(X^3\Phi) = 1.513\,843\,5(80)$ Å, using the relation $B_e = B_0 + \alpha_e/2$. Two years later Ram *et al.*¹⁹ by Fourier transform infrared spectroscopy determined $B_{0,\Omega=4}$ and $\alpha_e = 0.212\,444\,(93)$ cm^{-1} , thus $r_e(X^3\Phi_{\Omega=4}) = 1.531\,291\,(8)$ Å. The latter r_e ($\Omega = 4$) value, however, was “corrected” for spin–orbit effects by Tomonari *et al.*²⁶ through the formula $B_{0,\Omega} = B_0 + (2B_0^2/A\Lambda)\Sigma$, where $A = -242.7$ cm^{-1} is the experimental SO coupling constant;¹¹ Σ is the projection of the spin along the internuclear axis; 0, ± 1 in the present case. These authors obtained $r_e(X^3\Phi) = 1.5161$ Å,²⁶ practically equal to the value of Beaton *et al.*¹⁶ and equal to the $\Omega = 3$ value of Ram *et al.*,¹⁹ $r_e(X^3\Phi_{\Omega=3}) = 1.5170$ Å, which does not require any SO correction ($\Sigma = 0$). Finally, from the most recent determination of $B_{0,\Omega=4}$ and $B_{0,\Omega=3}$ parameters through Fourier transform infrared emission spectroscopy by Gordon *et al.*,²⁰ $r_e(X^3\Phi_{\Omega=4}) = 1.532\,664\,(16)$ Å and $r_e(X^3\Phi_{\Omega=3}) = 1.5181$ Å. The former value corrected for SO interaction gives $r_e(^3\Phi) = 1.5175$ Å equal to the bond distance of $^3\Phi_3$ ($\Sigma = 0$) component; see Ref. 26 for details. Therefore, the experimental bond distance r_e of the $X^3\Phi$ state of CoH is bracketed between 1.514 and 1.518 Å.²⁶

From Table II we can see that the bond distance of the $X^3\Phi$ state is $r_e = 1.517$ (1.519) [1.512] Å at the MRCI+Q (RCCSD(T)) [MRCI–L+Q] level of theory, in excellent agreement with the experimental value of 1.514 – 1.518 Å. Core subvalence effects change the above r_e numbers by less than 0.003 Å. Scalar relativistic effects, however, reduce the bond distance at all levels by ~ 0.013 Å, thus at the highest level of theory r_e converges to 1.500 Å; see Table II. Tomonari *et al.*²⁶ at their highest level of calculation, MRCPA(4), give $r_e(X^4\Phi) = 1.5066$ Å. Although the relativistic DKH2 effects reduce the bond length they are able to better predict the binding energy or spectroscopic parameters (ω_e). Therefore we are rather inclined to accept that the agreement of the r_e value with experiment at a lower level of theory (non-relativistic approach) could be a result of cancellation of errors. Since the relativistic approximation negatively affects the bond length a safe conclusion is that this approximation (although at a higher level than the non-relativistic one) still lacks these elements that would make it a better level of theory. That is, there are still certain internal imbalances with DKH calculations that would make them a “panacea” for computation.

Fig. 2 displays the first order MRCI/5 ζ SO splittings of the first 8 states of CoH, 4 triplets and 4 quintets. The SO coupling interaction in the $X^4\Phi_\Omega$ state lifts the Ω –degeneracy, giving rise to three $\Omega = 4, 3, 2$ components according to the relation $\Delta E = A \times \Lambda \times \Sigma$. The calculated SO coupling constant $|A| = 245.7$ cm^{-1} is in excellent agreement with the experimental value of -242.7 ± 1 cm^{-1} (Ref. 11) or -242.3 cm^{-1} (Ref. 20). We were unable, however, to calculate any significant equilibrium bond length differences between

TABLE II. Total energies E (E_h), bond distances r_e (\AA), dissociation energies D_e (kcal mol^{-1}), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm^{-1}), rotational-vibrational coupling constants α_e (cm^{-1}), and dipole moments μ (D) of the $X^3\Phi$ of CoH at various levels of theory.

Method ^a	$-E$	r_e	D_e^b/D_0^c	ω_e	$\omega_e x_e$	α_e	$\langle\mu\rangle/\mu_{FF}^d$
MRCI	1382.278 39	1.518	52.8/50.0	1869	34.9	0.230	3.01/3.00
MRCI+Q	1382.295 16	1.517		1914	31.5	0.245	/2.86
MRCI+DKH2	1392.717 02	1.502	48.9/45.9	1959	33.0	0.246	2.67/2.76
MRCI+DKH2+Q	1392.734 23	1.505		1938	35.1	0.237	/2.63
C-MRCI	1382.708 07	1.528	51.0/48.2	1812	35.5	0.237	3.08/3.17
C-MRCI+Q	1382.759 33	1.519		1867	31.8	0.216	/3.00
C-MRCI+DKH2	1393.146 61	1.507	46.6/43.7	1890	33.5	0.252	2.73/2.92
C-MRCI+DKH2+Q	1393.198 65	1.500		1932	37.8	0.230	/2.76
RCCSD(T)	1382.291 25	1.519	51.7/48.8	1913	30.6	0.215	/2.89
RCCSD(T)+DKH2	1392.730 05	1.505	47.7/44.7	1922	31.0	0.226	/2.61
C-RCCSD(T)	1382.769 40	1.516	53.1/50.3	1871	35.5	0.221	/2.80
C-RCCSD(T)+DKH2	1393.208 98	1.496	48.9/45.9	1934	33.4	0.234	/2.56
MRCI-L	1382.291 87	1.512	55.3/52.4	1896	36.1	0.223	2.95/2.87
MRCI-L+Q	1382.298 95	1.512		1900	35.6	0.218	/2.80
MRCI-L+DKH2	1392.731 18	1.499	51.7/48.7	1979	33.0	0.205	2.35/2.86
MRCI-L+DKH2+Q	1392.738 65	1.500		1994	33.2	0.202	/2.63
MCPF ^e		1.532	44.7 (=D _e)	1842			2.74
C-MRCPA ^f	~1382.647 ^g	1.5066		1929			3.23
Expt.		1.514–1.518 ^h	45.0 ± 1.2 ⁱ (=D ₀)	1926.7 ^j	34.6 ^j	0.219 74 ^j 0.212 444 ^l	1.88 ± 0.08 ^k

^a+Q, DKH2, and C- refer to the Davidson correction for unlinked clusters, Douglas-Kroll-Hess approximation of second order for scalar relativity, and that the sub-valence core electrons of Co ($3s^2 3p^6$) have been included in the CI. Calculations marked by “-L” (MRCI-L etc) have been performed with a larger reference space; see text.

^bWith respect to the ground state atoms, $a^4F + ^2S$.

^c $D_0 = D_e - \omega_e/2 + \omega_e x_e/4 - \text{BSSE}$.

^dDipole moment calculated as an expectation value $\langle\mu\rangle$, or through the finite-field approach, μ_{FF} ; field strength 10^{-5} a.u.

^eReference 23; MCPF/[8s6p4d3f/C₀4s3p_H] calculations.

^fReference 26; Core MRCPA/(9s7p5d2f1g)/C₀(5s3p1d)_H STOs.

^gObtained from Fig. 1 of Ref. 26.

^hSee text.

ⁱReference 18; ion beam thermochemistry; D₀ value.

^jReference 13; CO-Faraday laser magnetic resonance spectroscopy.

^kReference 21; optical Stark spectroscopy.

^lReference 19; Fourier transform emission spectroscopy.

the two Ω states $X^4\Phi_4$ and $X^3\Phi_3$, the $X^4\Phi_4$ (inverted) being the lowest by $737 (=3 \times A) \text{ cm}^{-1}$.

Recently, Steimle and co-workers²¹ measured the permanent electric dipole moment of the $X^3\Phi_4$ and $A' ^3\Phi_4$ states of CoH, $\mu = 1.88 \pm 0.08$ and 0.01 ± 0.08 D, respectively. Previous *ab initio* calculations for the $X^3\Phi$ state gave 2.74 (Ref. 23) and 3.23 D (Ref. 26) in stark disagreement with experiment. Our calculated μ values of the $X^3\Phi$ state either by the expectation ($\langle\mu\rangle$) or the finite-field (μ_{FF}) approach, and at all levels of theory, are significantly larger than 2 D; see Table II. In particular, the μ_{FF} C-MRCI+DKH2+Q (C-RCCSD(T)+DKH2) [MRCI-L+DKH2+Q] values are 2.76 (2.56) [2.63] D, with corresponding expectation values at the C-MRCI+DKH2 [MRCI-L+DKH2] level, $\langle\mu\rangle = 2.73$ [2.35] D. Presuming that the experimental number is correct, our best value is 2.35 D, still differing by +0.4 D from experiment. Interestingly, at the highest level of theory (MRCI-L+DKH2+Q), $\mu_{FF} = 2.63$ D. It should be mentioned also that the SO interaction does not seem to affect the dipole moment of CoH. Notwithstanding the difficulties of calculating accurately electric dipole moments, it is our belief that there might be something wrong with the experimental dipole moment of the $X^3\Phi$ state of CoH since at all levels of calculation it is found larger than the experimental one.

We would like now to discuss the bonding character of CoH. The $X^3\Phi$ state correlates adiabatically to

$\text{Co}(a^4F; 4s^2 3d^7) + \text{H}(^2S)$, diabatically, however, to $\text{Co}(b^4F; 4s^1 3d^8) + \text{H}(^2S)$, (experimentally) 0.417 eV higher. The dominant equilibrium MRCI (or CASSCF) configurations and Mulliken atomic populations are (counting the outer 10 e^- only), are

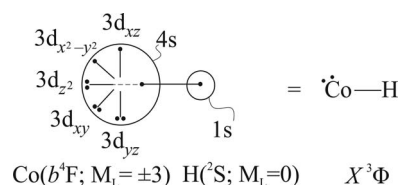
$$|X^3\Phi\rangle_{B_1} \approx 0.66(|1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^2 1\delta_+^1 1\delta_-^1\rangle + |1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^1 1\delta_+^1 1\delta_-^1\rangle) \\ 4s^{0.99} 4p_z^{0.09} 3d_{z^2}^{1.71} 3d_{xz}^{1.50} 3d_{yz}^{1.50} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.50} / \text{Co } 1s^{1.17} / \text{H}$$

with the composition of the 1σ (“bonding”) natural orbital and its orthogonal counterpart 2σ being,

$$1\sigma \approx (0.60) 4s + (0.59) 1s - (0.28) 3d_{z^2}, \quad \text{and}$$

$$2\sigma \approx (0.87) 3d_{z^2} + (0.49) 1s.$$

The bonding is captured by the following valence-bond-Lewis (vbL) diagram



With no doubt the negative end of the molecule is on the H atom, the result of a Co-to-H charge transfer of ~ 0.2 electrons from the $3d_{z^2}$ Co orbital. A Co-to-H electron charge transfer is expected, considering that the *in situ* ionization energy of Co is much smaller than that of the H atom, $7.86 - 0.42 = 7.44$ eV vs 13.60 eV.

2. $A^3\Delta$, $B^3\Pi$, $C^3\Sigma^-$

All 26 higher states have been calculated at the plain MRCI(MRCI+Q)/5 ζ level. The three lowest states above correlate adiabatically to $\text{Co}(a^4F) + \text{H}(^2S)$, diabatically, however, to $\text{Co}(b^4F) + \text{H}(^2S)$; see Fig. 1. At the MRCI level they are located at $T_e(^3\Delta, ^3\Pi, ^3\Sigma^- \leftarrow X^3\Phi) = 2188, 2857,$ and 3097 cm^{-1} , respectively, the $^3\Sigma^-$ state being the lowest. The +Q correction suppresses significantly the energy separation(s), while rendering them degenerate within an energy range $\Delta T_e (\Delta T_0) = 39 (75)$ cm^{-1} , i.e., $T_e (T_0 = T_e + \Delta\omega_e/2) = (C^3\Sigma^-, B^3\Pi, A^3\Delta \leftarrow X^3\Phi) = 1813 (1742), 1836 (1778),$ and $1844 (1817)$ cm^{-1} , respectively, the $^3\Sigma^-$ being now the highest; see Table III. Of course the A, B, and C labeling based on the MRCI+Q results is formal. From now on we disregard the $\Delta\omega_e/2$ zero point energy differences, unimportant after including the +Q correction. The SO interaction lifts the degeneracy of the Ω components of the $A^3\Delta$ and $B^3\Pi$ states, the calculated (not known experimentally) SO coupling constant being $|A| = 242$ and 246 cm^{-1} , respectively. Assuming a negative A for both states (inverted), the resulting energy level diagram of $^3\Delta_{3,2,1}, ^3\Pi_{2,1,0\pm}$, and $^3\Sigma^-$ states is shown in Fig. 2. An $\Omega'' = 3 \leftarrow X^3\Phi_4$ transition at 2469 ± 3 cm^{-1} observed by Varberg *et al.*¹¹ through laser rotational spectroscopy, was tentatively assigned to a $^3\Delta_3$ state. Our calculated $^3\Delta_3 \leftarrow X^3\Phi_4$ transition is $1813 (\text{MRCI+Q}) + 737 - 484 = 2066$ cm^{-1} in acceptable agreement with experiment, hence, confirming the experimental assignment.

3. $a^5\Phi$, $b^5\Sigma^-$, $c^5\Pi$, $d^5\Delta$

This bundle of four quintets, also correlating diabatically to the second channel, is well separated from the triplets with a mean MRCI+Q energy distance $\bar{T}_e \approx 8000$ cm^{-1} and covering an energy range of ~ 2000 cm^{-1} ; see Fig. 1. We are rather confident that the spectroscopic labeling a, b, c, and d is correct. Through laser photoelectron spectroscopy we do know that a state tentatively assigned to $a^5\Phi$ is located at $T_0 = 6625 \pm 100$ cm^{-1} with $r_e = 1.67 \pm 0.05$ Å.⁸ The MRCI+Q r_e and T values of the $a^5\Phi$ are (Table III), $r_e = 1.636$ Å and $T_e(T_0) = 6961(6834)$ cm^{-1} in very good agreement with experiment, therefore confirming the tentative assignment to $^5\Phi$. Corresponding values at the MRCPA(4) level by Tomonari *et al.*²⁶ are, $r_e = 1.6320$ Å and $T_e = 6331$ cm^{-1} , similar to the present ones. Fig. 2 shows the effect of the SO interaction to the $a^5\Phi$, $c^5\Pi$, and $d^5\Delta$ states, all splitting in five Ω components; the calculated SO coupling constants are, $|A| = 133.7, 134,$ and 135 cm^{-1} for the a, c, and d states, respectively.

4. Higher states

The MRCI+Q/5 ζ PECs of 19 higher states are shown in Fig. 1 while numerical results are listed in Table III.

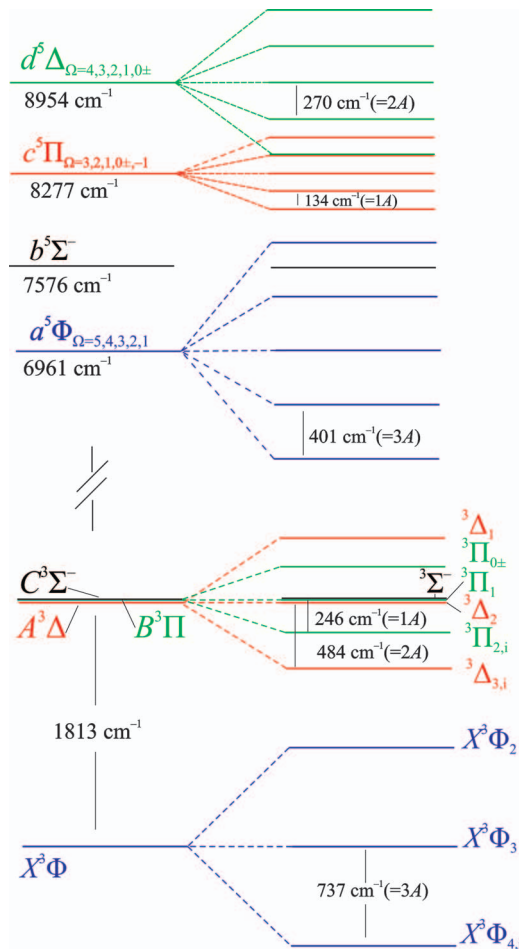


FIG. 2. MRCI/5 ζ spin orbit splittings of the first eight states of CoH. A is the spin orbit coupling constant.

Experimental results are available for two states, one correlating to the second channel (labeled $A^3\Phi$ by the experimentalists and $2^3\Phi$ in the present work), and a second one correlating adiabatically to the third channel (labeled $A^3\Phi$ by the experimentalists and $3^3\Phi$ here); see Tables I and III and Fig. 1. The leading equilibrium MRCI configurations of the $2(A^3)\Phi$ state are

$$\begin{aligned}
 |2(A^3)\Phi\rangle_{B1} \approx & 0.49 |1\sigma^2 2\sigma^1 \bar{3}\sigma^1 1\pi_x^2 1\pi_y^1 1\delta_+^2 1\delta_-^1\rangle \\
 & + 0.49 |1\sigma^2 2\sigma^1 \bar{3}\sigma^1 1\pi_x^1 1\pi_y^2 1\delta_+^1 1\delta_-^2\rangle \\
 & - 0.36 |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^2 \bar{1}\pi_y^1 1\delta_+^2 1\delta_-^1\rangle \\
 & - 0.27 |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^2 1\pi_y^1 1\delta_+^1 \bar{1}\delta_-^1\rangle.
 \end{aligned}$$

The bonding electrons are hosted by the 1σ orbital with the six $(d_{xy})^3 (d_{xz})^3$ electrons being indifferent to bonding.

Experimentally the $A^3\Phi$ state is located ~ 12500 cm^{-1} above the X-state at $r_0 = 1.6352$ Å, the latter obtained from the $B_0 = 6.36226(49)$ cm^{-1} rotational constant of Gordon *et al.*²⁰ From the high resolution emission spectroscopy study of these workers we know that $T_0(X^3\Phi_4 \rightarrow A^3\Phi_4) = 12358.4390 (85)$ and $T_0(X^3\Phi_4 \rightarrow A^3\Phi_3) = 12644.977 (18)$ cm^{-1} . Assuming that the $A^3\Phi_3$ state is not affected from the

TABLE III. Total energies E (E_h), bond distances r_e (\AA), dissociation energies D_e (kcal mol^{-1}), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm^{-1}), rotational-vibrational coupling constants α_e (cm^{-1}), dipole moments μ (D), Mulliken charges on Co, q_{Co} , and energy separations, T_e (cm^{-1}) for 27 states of Co^1H at the MRCI+Q/5 ζ level of theory.

State ^a	-E	r_e	D_e ^b	ω_e	$\omega_e x_e$	α_e	$\langle \mu \rangle / \mu_{\text{FF}}^c$	q_{Co}	T_e
X $^3\Phi$ (a^4F)	1382.295 16	1.517	52.8	1914	31.5	0.245	3.01/2.86	0.20	0.0
A $^3\Delta$ (a^4F)	1382.286 90	1.550	43.7	1772	28.8	0.188	3.18/3.36	0.20	1813
$^3\Delta_3$ (Expt.) ^d									2469 \pm 3
B $^3\Pi$ (a^4F)	1382.286 80	1.544	44.8	1797	32.4	0.214	3.05/3.40	0.21	1836
C $^3\Sigma^-$ (a^4F)	1382.286 76	1.510	47.3	1860	32.3	0.219	2.42/2.61	0.17	1844
a $^5\Phi$ (a^4F)	1382.263 45	1.636	34.5	1659	31.9	0.184	0.78/0.88	0.26	6961
C-MRCPA ^e		1.6320		1756					6331
a $^5\Phi$ (Expt.) ^f		1.67 \pm 0.05							6625 \pm 110 (T_0)
b $^5\Sigma^-$ (a^4F)	1382.260 64	1.624	34.2	1679	23.5	0.186	0.72/0.89	0.27	7576
c $^5\Pi$ (a^4F)	1382.257 45	1.652	31.1	1619	33.5	0.190	0.82/0.91	0.25	8277
d $^5\Delta$ (a^4F)	1382.254 37	1.673	28.6	1628	54.7	0.187	0.91/0.73	0.29	8954
2 $^3\Pi$ (b^4F)	1382.242 48	1.658	36.4	1579	34.1	0.193	0.73/0.66	0.27	11 563
2 ($=A'$) $^3\Phi$ (b^4F)	1382.242 17	1.661	36.8	1580	31.8	0.187	0.59/0.43	0.28	11 630
A $^3\Phi_4$ (Expt.)							0.01 \pm 0.08 ^h		12 358.4 ^g
A $^3\Phi_3$ (Expt.)		1.6352 ($=r_0$) ^g							12 645.0 ^g
2 $^3\Sigma^-$ (b^4F)	1382.239 04	1.667	34.7	1542	30.6	0.182	1.02/0.88	0.27	12 317
2 $^3\Delta$ (b^4F)	1382.236 98	1.688	33.5	1578	33.2	0.187	0.66/0.44	0.29	12 769
1 $^1\Pi$ (a^2F)	1382.236 24	1.527	43.7	1839	33.3	0.224	3.24/3.13	0.21	12 933
1 $^1\Sigma^+$ (a^2D)	1382.235 50	1.496	71.2	1983	23.2	0.144	2.52/3.11	0.18	13 094
1 $^1\Delta$ (a^2F)	1382.229 35	1.456	37.4	2056	25.5	0.190	0.70/2.65	0.14	14 444
1 $^1\Gamma$ (a^2G)	1382.219 87	1.465	55.2	2008	24.0	0.215	2.11/2.68	0.15	16 525
2 $^5\Sigma^-$ (b^4F)	1382.208 74	1.613	15.8	1732	26.4	0.210	0.53/0.96	0.28	18 968
1 $^1\Phi$ (a^2F)	1382.204 50	1.514	23.1	1879	34.7	0.216	3.19/2.83	0.20	19 898
3 $^3\Delta$ (a^2F)	1382.201 74	1.547	21.1	1875	35.5	0.207	0.17/0.59	0.21	20 504
2 $^5\Pi$ (b^4F)	1382.193 94	1.631	6.8	1599	32.1	0.239	0.79/0.69	0.21	22 215
3 ($=A'$) $^3\Phi$ (a^2F)	1382.191 03	1.582	15.5	1747	38.6	0.216	0.15/0.55	0.22	22 854
A $^3\Phi_4$ (Expt.) ^g		1.6154 ($=r_0$)							22 243.2 (T_0)
3 $^3\Pi$ (a^2F)	1382.186 94	1.560	13.0	1662	27.3	0.224	0.25/0.36	0.24	23 753
1 $^3\Sigma^+$ (a^2D)	1382.179 53	1.623	38.6	1665	30.7	0.171	0.48/0.59	0.27	25 378
3 $^5\Pi$ (a^4P)	1382.177 00	1.527	21.7	1824	33.8	0.109	1.93/1.91	0.20	25 934
1 $^3\Gamma$ (a^2G)	1382.172 74	1.629	27.8	1603	29.4	0.179	0.58/0.99	0.26	26 869
1 $^1\Sigma^-$ (a^2F)	1382.171 40	1.564	4.0	1767	39.1	0.191	0.63/1.16	0.19	27 161
4 $^3\Delta$ (a^2D)	1382.158 96	1.666	23.9	1643	32.2	0.183	0.59/1.72	0.27	29 894

^aValues in parentheses after the molecular term symbol denote the end term of Co atom.

^bAdiabatic D_e values at the MRCI/5 ζ level.

^cDipole moments calculated as expectation values (μ), or through the finite-field approach, μ_{FF} ; field strength 10^{-5} a.u.

^dReference 11; rotational spectroscopy.

^eReference 26; core MRCPA/(9s7p5d2f1g)/Co(5s3p1d)_H STOs.

^fReference 8; photoelectron spectroscopy.

^gReference 20; near infrared emission spectroscopy; [$A'^3\Phi_4(v=0)$, $A'^3\Phi_3(v=0)$] \rightarrow $X^3\Phi_4(v=0)$.

^hReference 21; Dipole moment of the $A'^3\Phi_4$ state; optical Stark spectroscopy.

SO interaction to first order ($\Sigma = 0$), our calculated energy separation is $T_0(X^3\Phi_4 \rightarrow 2(A')^3\Phi_3) = T_e(\text{MRCI+Q}) + 3 \times A + \Delta\omega_e/2 = 11\,630 + 737 - (1914 - 1580)/2 = 12\,200 \text{ cm}^{-1}$, in very good agreement with the $X^3\Phi_4 \rightarrow A'^3\Phi_3$ experimental value. On the other hand, the calculated MRCI(+Q) bond distance, $r_e = 1.648(1.661) \text{ \AA}$, is by 0.02–0.03 \AA longer than the experimental value.

It is remarkable that the experimental electric dipole moment of the $A'^3\Phi_4$ state is nearly zero, $\mu = 0.01 \pm 0.08 \text{ D}$.²¹ Our MRCI and MRCI+Q expectation and finite field μ values of the $2(A')^3\Phi$ state are, $\langle \mu \rangle = 0.59$ and $\mu_{\text{FF}} = 0.43 \text{ D}$, respectively. Considering the finite field value as more trustworthy,⁵⁵ the calculated number is at least 0.3 D higher than the experiment, a discrepancy analogous to that of the ground state dipole moment (*vide supra*). The MRCI Mulliken atomic pop-

ulations and the form of the three σ orbitals of the $2(A')^3\Phi$ state are

$$4s^{0.88}4p_z^{0.52}3d_z^{1.32}3d_{xz}^{1.50}3d_{yz}^{1.50}3d_{x^2-y^2}^{1.50}3d_{xy}^{1.50}/1s^{1.25},$$

$$1\sigma \approx (0.38)4s + (0.36)3d_{z^2} + (0.51)1s,$$

$$2\sigma \approx (0.35)4p_z - (0.81)3d_{z^2} + (0.27)1s,$$

$$3\sigma \approx (0.72)4s - (0.39)4p_z - (0.41)3d_{z^2}.$$

The $X^3\Phi$ and $2(A')^3\Phi$ dominant configurations differ by a $2\sigma^2 \rightarrow 2\sigma^1 3\sigma^1$ excitation, reflected to an increase by $\sim 0.4 e^-$ in the $4p_z$ Co population of the $2(A')^3\Phi$ state. As was mentioned the $1\sigma^2$ is a bonding distribution, with the 2σ and 3σ orbitals responsible for transferring electron density in the back of the Co atom, thus diminishing drastically the dipole

moment of the $2(A')^3\Phi$ state as compared to the $X^3\Phi$. Nevertheless, the ionic character of this state is significant, the total Co–to–H Mulliken charge transfer being $\sim 0.3 e^-$. For the $A^3\Phi_4$ state ($3^3\Phi_3$ in Table III), Gordon *et al.*²⁰ give $B_0 = 6.5197(14) \text{ cm}^{-1}$, thus $r_0 = 1.6154 \text{ \AA}$, and $T_0(X^3\Phi_4 \rightarrow A^3\Phi_4) = 22\,243 \text{ cm}^{-1}$. The corresponding calculated MRCI+Q numbers are $r_e = 1.582 \text{ \AA}$ and $T_0(X^3\Phi \rightarrow 3(A)^3\Phi) = T_e + \Delta\omega_e/2 = 22\,770 \text{ cm}^{-1}$, in accord with experiment. The predicted dipole moment $\langle \mu \rangle$ ($\mu_{\text{FF}} = 0.15(0.55) \text{ D}$) is quite small, one of the smallest of all studied states; see Table III. An $\Omega = 4$ state located above the $A^3\Phi$ was also observed for the CoD isotopomer by Gordon *et al.*²⁰ at $T \sim 13\,500 \text{ cm}^{-1}$, and tentatively assigned to a $1^1\Gamma_4$ state based on the theoretical results of Freindorf *et al.*²⁴ Our calculations predict a $1^1\Gamma$ state correlating adiabatically to $\text{Co}(a^2G; 4s^23d^7) + \text{H}(^2S)$, located at $T_e(^1\Gamma-X^3\Phi) = 16\,525 \text{ cm}^{-1}$, about 4000 cm^{-1} above the $2(A')^3\Phi$ state. The $1^1\Gamma$ state is well bound with $D_0 = 52.3 \text{ kcal/mol}$, $r_e = 1.465 \text{ \AA}$, $\omega_e = 2008 \text{ cm}^{-1}$, and $\mu_{\text{FF}} = 2.68 \text{ D}$; see Table III. Corresponding values from Ref. 24 are $T(^1\Gamma-X^3\Phi) = 18\,551 \text{ cm}^{-1}$, $r_e = 1.418 \text{ \AA}$, and $\omega_e = 2157 \text{ cm}^{-1}$.

MRCI results for all states of CoH are given in Table S1, while Tables S2 and S3 list MRCI leading CFs functions and Mulliken atomic populations.⁵⁷

B. CoH⁺

The ground state of Co^+ is $a^3F(3d^8)$ with the first $a^5F(4s^13d^7)$ and second $b^3F(4s^13d^7)$ excited states 0.429 and 1.212 eV higher.⁵⁴ The interaction of $\text{Co}^+(a^3F, b^3F) + \text{H}(^2S)$ gives rise to 16 ($=8+8$) $2S+1\Lambda$ states, doublets and quartets, namely, $2^4(\Sigma^-, \Pi, \Delta, \Phi)$. From the second channel, $\text{Co}^+(a^5F) + \text{H}(^2S)$, we also get 8 states of $\Sigma^-, \Pi, \Delta,$ and Φ symmetry, quartets and sextets. We have calculated all 8 PECs correlating adiabatically to the first channel, $\text{Co}^+(a^3F) + \text{H}(^2S)$, the 4 quartets correlating to the second channel (the 4 sextets are repulsive), and all but two quartets ($4^1\Pi, 4^1\Phi$) emanating from the third channel. Six more PECs related to higher excited states of Co^+ have also been constructed, i.e., ($I^2\Sigma^+, 3^2\Pi$), $4^2\Pi$, $I^2\Gamma$, $2^2\Gamma$, and I^2H correlating adiabatically to $\text{Co}^+(a^1D, a^3P, a^1G, a^3G, a^3H) + \text{H}(^2S)$, respectively; see Fig. 3. It is clear that the $3d^8$ configuration of the a^3F ground term of Co^+ precludes the formation of a *bona fide* Co^+-H chemical bond. The $4s^13d^7$ configuration of Co^+ , conducive to bond formation, relates to the first two excited channels (a^5F, b^3F) + $\text{H}(^2S)$. Therefore the first four states of CoH^+ all of quartet multiplicity, $X^4\Phi, A^4\Sigma^-, B^4\Pi,$ and $C^4\Delta$ (*vide infra*), correlate diabatically to $\text{Co}^+(a^5F) + \text{H}(^2S)$. *Mutatis mutandis*, the corresponding four doublets correlate diabatically to the third channel, $\text{Co}(b^3F) + \text{H}(^2S)$, whereas the four quartets of this channel should have repulsive character and indeed this is the case; see Fig. 3.

1. $X^4\Phi, A^4\Sigma^-, B^4\Pi, C^4\Delta$

Quite interestingly the ground state of CoH^+ has not been determined experimentally; the only experimental result on CoH^+ is the binding energy, $D_0^0 = 47 \pm 2$ (Refs. 10 and 33) or

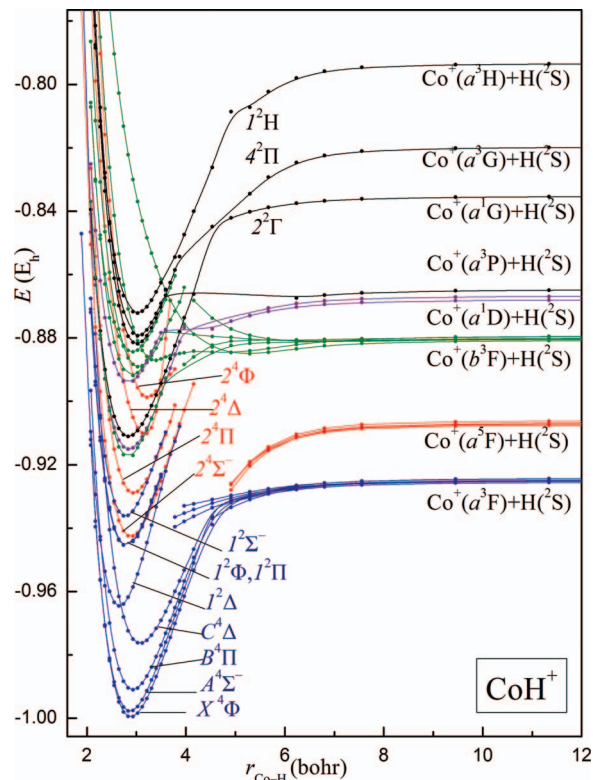


FIG. 3. MRCI+Q/5 ζ PECs of 24 states of CoH^+ .

$42 \pm 4 \text{ kcal/mol}$,¹⁴ both numbers from the Armentrout group. Based on the $47 \pm 2 \text{ kcal/mol}$ value, apparently more accurate, we get $\text{IE}(\text{CoH}) = 7.8 \pm 0.1 \text{ eV}$ (*vide supra*), practically equal to the ionization energy of the Co atom, 7.864 eV .⁵⁴ According to our calculations the $4^1\Phi$ is indeed the ground state, but a $4^1\Sigma^-$ state lies just above it (but see below).

The leading equilibrium CFs of the $X^4\Phi$ state are identical to those of the $X^3\Phi$ of CoH, after the removal of an electron from the 2σ doubly occupied orbital of the latter ($2\sigma^2 \rightarrow 2\sigma^1$), with the following MRCI Mulliken atomic populations

$$4s^{0.68}4p_z^{0.10}3d_{z^2}^{1.21}3d_{xz}^{1.50}3d_{yz}^{1.50}3d_{x^2-y^2}^{1.50}3d_{xy}^{1.50}/1s^{0.98}.$$

Clearly the $X^4\Phi$ state is obtained from the $X^3\Phi$ (CoH) by removing an electron from the $3d_{z^2}$ ($\approx 2\sigma$) orbital; see the vbL diagram of the $X^3\Phi$ state of CoH. The bond is formed by singlet coupling of the $4s3d_{z^2}$ hybrid on Co^+ to the $1s$ orbital of H; obviously the six $3d_{\pi^3}3d_{\delta^3}$ electrons are not involved in the bonding. Calculated numerical results for the $X^4\Phi$ state of CoH^+ are listed in Table IV. At the MRCI (RCCSD(T)) level, combined core ($3s^23p^6$) and scalar relativistic effects reduce the bond distance by 0.006 (0.017) \AA and increase the binding energy by 5.4 (4.1) kcal/mol . Notice also that both effects in both methods are practically additive. The C–MRCI+DKH2 (C–RCCSD(T)+DKH2) dissociation energy is $D_0 = 49.6$ (43.0) kcal/mol at r_e (including +Q) = 1.521 (1.514) \AA . We believe that the multireference approach is more accurate for the system at hand, therefore, our recommended values are $r_e = 1.521 \text{ \AA}$, $D_e(D_0) = 52.3$ (49.6) kcal/mol , and $\omega_e = 1912 \text{ cm}^{-1}$. The C–MRCI+DKH2+Q (C–RCCSD(T)+DKH2) calculated ionization energy of CoH

TABLE IV. Total energies E (E_h), bond distances r_e (\AA), dissociation energies D_e (kcal mol^{-1}), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm^{-1}), and rotational–vibrational coupling constants α_e (cm^{-1}), of the $X^4\Phi$ of CoH^+ at various levels of theory.

Method ^a	$-E$	r_e	D_e^b/D_0^c	ω_e	$\omega_e x_e$	α_e
MRCI	1381.98725	1.536	46.9/44.2	1897	34.3	0.207
MRCI+Q	1381.99962	1.527		1924	33.6	0.207
MRCI+DKH2	1392.42693	1.533	54.8/52.1	1903	35.5	0.213
MRCI+DKH2+Q	1392.43940	1.524		1930	34.7	0.212
C–MRCI	1382.41573	1.538	44.2/41.5	1862	35.2	0.214
C–MRCI+Q	1382.45943	1.523		1903	33.9	0.215
C–MRCI+DKH2	1392.85639	1.535	52.3/49.6	1871	36.5	0.220
C–MRCI+DKH2+Q	1392.90034	1.521		1912	35.2	0.220
RCCSD(T)	1381.99990	1.531	41.7/38.9	1936	33.1	0.198
RCCSD(T)+DKH2	1392.43924	1.526	49.1/46.3	1946	33.9	0.204
C–RCCSD(T)	1382.47368	1.519	38.4/35.6	1955	32.9	0.205
C–RCCSD(T)+DKH2	1392.91392	1.514	45.8/43.0	1965	33.7	0.210
Expt.			47 ± 2 ($=D_0$) ^d			
			42 ± 4 ($=D_0$) ^e			
MRCI+Q ^f		1.504	56.9 ($=D_0$)	2005		

^aSee Table I for explanation of acronyms and symbols.

^bWith respect to the ground state atoms, $\text{Co}(a^3F) + \text{H}(^2S)$.

^c $D_0 = D_e - \omega_e/2 + \omega_e x_e/4$.

^dReferences 10 and 33.

^eReference 14.

^fReference 38; MRCI+Q/[6s5p3d1f/_{Co}aug–cc–pVTZ/H] with Stuttgart relativistic small core ($1s^2 2s^2 2p^6 /_{Co}$) effective potential.

is, $IE = 8.12$ (8.03) eV in quite good agreement with the “experimental” value of 7.9 ± 0.1 eV.

The first order SO interaction splits the $X^4\Phi_\Omega$ state into four Ω components, $\Omega = 9/2, 7/2, 5/2$, and $3/2$, with a MRCI calculated SO constant $|A| = 179.8 \text{ cm}^{-1}$ and $\Delta E(\Delta\Omega = 1) = A \times \Delta \times (\Delta\Sigma) = 3A = 539.4 \text{ cm}^{-1}$. Thus the SO interaction lowers the energy of the $X^3\Phi$ state by $9/2A = 809 \text{ cm}^{-1}$. Assuming that A is negative as in the $X^3\Phi$ state of CoH (inverted), the ground state of CoH^+ is $^4\Phi_{9/2}$. All higher states have been examined at the MRCI(+Q) level, including the next three quartets, $A^4\Sigma^-$, $B^4\Pi$, and $C^4\Delta$ located at $T_e = 815$ (395), 1977 (1881), and 5245 (5104) cm^{-1} , respectively, correlating adiabatically [diabatically] to $\text{Co}^+(a^3F) + \text{H}(^2S)[\text{Co}^+(a^5F) + \text{H}(^2S)]$; see Table V and Fig. 3. The SO coupling constants are $|A| = 181.0$ ($B^4\Pi$) and 182.4 ($C^4\Delta$) cm^{-1} . Although the MRCI+Q $A^4\Sigma^- - X^4\Phi$ energy separation is just 395 cm^{-1} , including the SO interaction we get $T_e(A^4\Sigma^- - X^4\Phi_{9/2}) = 395 + 4.5 \times A$ ($X^4\Phi$) = $395 + 809 = 1204 \text{ cm}^{-1}$. On the other hand the $^4\Phi_{3/2}$ component lies $4.5 \times A - 395 = 414 \text{ cm}^{-1}$ above the $A^4\Sigma^-$ state. The A, B , and C states are well bound with MRCI+Q bond distances and (MRCI) binding energies, $r_e = 1.519, 1.548, 1.628 \text{ \AA}$ and $D_e = 45.2, 41.4, 31.6 \text{ kcal/mol}$, respectively (Table V). Assuming that core subvalence and relativistic effects follow similar trends as in the $X^4\Phi$ state, better estimates of r_e and D_e values can be obtained by decreasing the former by 0.006 – 0.007 \AA and increasing the latter by $\sim 5 \text{ kcal/mol}$ (*vide supra*), thus $r_e = 1.51, 1.54, 1.62 \text{ \AA}$ and $D_e = 50, 46, 37 \text{ kcal/mol}$ for the A, B , and C states, respectively.

2. $1^2\Delta, 1^2\Phi, 1^2\Pi, 1^2\Sigma^-$

The four doublets above are related adiabatically to the first channel ($a^3F + ^2S$), diabatically, however, to the third

channel, i.e., $\text{Co}^+(b^3F) + \text{H}(^2S)$; see Fig. 3. The second channel, $a^5F + ^2S$, is precluded because it gives rise to quartets and sextets (*vide supra*); see Fig. 3. At the MRCI+Q level $T_e = 7685, 11878, 11886$, and 13910 cm^{-1} for the $1^2\Delta, 1^2\Phi, 1^2\Pi$, and $1^2\Sigma^-$ states, respectively. Observe that the $1^2\Phi$ and $1^2\Pi$ states are degenerate at the MRCI+Q level. The MRCI SO coupling constant is $|A| = 475.0$ ($1^2\Delta$), 318.2 ($1^2\Phi$), and 801.3 ($1^2\Pi$) cm^{-1} . The $1^2\Delta_{3/2,5/2}, 1^2\Phi_{7/2,5/2}$, and $1^2\Pi_{3/2,1/2}$ Ω components split by $2 \times A$ ($=950$), $3 \times A$ ($=954.6$), and $1 \times A$ ($=801.3$) cm^{-1} , respectively. Notice that the SO interaction lifts the degeneracy of the $1^2\Phi$ and $1^2\Pi$ states. The MRCI binding energies with respect to the ground state atoms [with respect to $b^3F + ^2S, 1.151$ (1.212) eV higher at the supermolecule MRCI(Expt⁵⁴) level] for the $1^2\Delta, 1^2\Phi, 1^2\Pi$, and $1^2\Sigma^-$ states are 19.1 [45.6], 10.4 [36.9], 8.8 [35.3], and 4.2 [30.7] kcal/mol, respectively. All four doublets have quite shorter MRCI+Q bond distances from the X -state, while the $1^2\Delta$ with $r_e = 1.405 \text{ \AA}$, has the shortest bond length of all studied states of CoH^+ ; see Table V.

3. Higher states

Numerical data for 16 higher states are collected in Table V. The next four quartets, $2^4\Sigma^-, 2^4\Pi, 2^4\Delta$, and $2^4\Phi$, correlate adiabatically to the second channel, $a^5F + ^2S$, diabatically, however, to the third one, $b^3F + ^2S$ (Fig. 3). Their MRCI adiabatic(diabatic) binding energies and MRCI+Q bond distances are 17.2 (34.3), 9.6 (26.7), -10.2 (6.9), and -11.2 (5.9) kcal/mol and $1.528, 1.554, 1.679$, and 1.700 \AA , respectively.

MRCI results for all states of CoH^+ are given in Table S4, while Tables S5 and S6 list MRCI dominant CFs and Mulliken atomic populations.⁵⁷

TABLE V. Total energies E (E_h), bond distances r_e (\AA), dissociation energies D_e (kcal mol^{-1}), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm^{-1}), rotational–vibrational coupling constants α_e (cm^{-1}), Mulliken charges on Co, q_{Co} , and energy separations, T_e (cm^{-1}) for 24 states of CoH^+ at the MRCI+Q/5 ζ level of theory.

State ^a	$-E$	r_e	D_e ^b	ω_e	$\omega_e x_e$	α_e	q_{Co}	T_e
$X^4\Phi$ (a^3F)	1381.999 62	1.527	46.9	1924	33.6	0.207	1.01	0.0
$A^4\Sigma^-$ (a^3F)	1381.997 82	1.519	45.2	1946	33.7	0.188	1.00	395
MRCI+Q ^c		1.499	56.0(D_0)	1992				
$B^4\Pi$ (a^3F)	1381.991 05	1.548	41.4	1882	34.9	0.189	1.02	1881
MRCI+Q ^c		1.534	51.3(D_0)	1910				
$C^4\Delta$ (a^3F)	1381.976 37	1.628	31.6	1742	47.4	0.205	1.02	5104
MRCI+Q ^c		1.597	44.4(D_0)	1803				
$I^2\Delta$ (a^3F)	1381.964 61	1.405	19.1	2308	38.9	0.225	0.96	7685
$I^2\Phi$ (a^3F)	1381.945 50	1.479	10.4	2078	37.0	0.194	0.95	11 878
$I^2\Pi$ (a^3F)	1381.945 47	1.472	8.8	1890	103.1	0.681	0.96	11 886
$2^4\Sigma^-$ (a^5F)	1381.942 63	1.528	17.2	1950	30.2	0.209	1.01	12 509
$I^2\Sigma^-$ (a^3F)	1381.936 25	1.470	4.2	2060	42.0	0.208	0.94	13 910
$2^4\Pi$ (a^5F)	1381.928 93	1.554	9.6	1929	33.7	0.176	0.98	15 516
$2^2\Pi$ (b^3F)	1381.917 61	1.509	19.9	2150	179.3	0.135	1.00	17 999
$I^2\Sigma^+$ (a^1D)	1381.915 09	1.505	30.1	1842	36.7	0.236	1.01	18 553
$I^2\Gamma$ (a^1G)	1381.911 08	1.499	47.9	1818	30.3	0.250	1.00	19 433
$2^4\Delta$ (a^5F)	1381.910 28	1.679	d				0.90	19 609
$2^4\Phi$ (a^5F)	1381.898 81	1.700	d				0.84	22 126
$3^2\Pi$ (a^1D)	1381.894 17	1.499	14.7	1811	47.2	0.258	0.99	23 143
$2^2\Phi$ (b^3F)	1381.891 92	1.537	4.8	1844	38.7	0.208	1.01	23 637
$2^2\Delta$ (b^3F)	1381.889 14	1.608	3.2	1763	38.2	0.183	1.03	24 247
$3^4\Sigma^-$ (b^3F)	1381.887 17	1.791	2.4	398($\Delta G_{1/2}$)			0.86	24 680
$3^4\Delta$ (b^3F)	1381.885 07	2.761	1.7	436	35.2	0.086	0.96	25 142
$2^2\Sigma^-$ (b^3F)	1381.884 44	1.545	0.4	1714	28.6	0.122	1.03	25 279
$2^2\Gamma$ (a^3G)	1381.881 92	1.591	36.7	1935	39.4	0.180	1.02	25 832
$4^2\Pi$ (a^3P)	1381.879 38	1.607	10.8	1919	37.2	0.157	1.04	26 390
I^2H (a^3H)	1381.872 21	1.595	47.7	1780	34.9	0.198	1.01	27 964

^aValues in parentheses after the molecular term symbol denote the end term of Co.

^bAdiabatic D_e values at the MRCI/5 ζ level.

^cReference 38; MRCI+Q/[6s5p3d1f/ $c_{\text{Co}}\text{aug-cc-pVTZ/H}$] with Stuttgart relativistic small core ($1s^22s^22p^6/c_{\text{Co}}$) effective potential; D_0 value.

^dUnbound with respect to their adiabatic channel, $\text{Co}^+(a^3F) + \text{H}(^2S)$.

C. CoH^-

The electron affinities of H and Co atoms are $EA = 0.7542$ (Ref. 42) and 0.662 ± 0.01 eV,⁴⁶ respectively, therefore the lowest adiabatic channel of CoH^- is $\text{Co}(a^4F; 4s^23d^7) + \text{H}^-(^1S)$. At this point it is useful to be reminded that H^- has only one bound state.⁵⁶ The interaction of $\text{Co}(a^4F) + \text{H}^-$ gives rise to four molecular quartets, $^4\Sigma^-$, $^4\Pi$, $^4\Delta$, and $^4\Phi$, clearly of repulsive character. The next energy channel, $\text{Co}^-(^3F; 4s^23d^8) + \text{H}(^2S)$, lies (experimentally) $0.7542 - 0.662 \pm 0.01 = 0.10$ eV higher. Notice that at the MRCI+Q level the calculated EA of Co is 0.42 eV. The more prone to bonding $\text{Co}^-(^3F) + \text{H}$ interaction results to 8 states, i.e., $2^4\Sigma^-$, $2^4\Pi$, $2^4\Delta$, and $2^4\Phi$, doublets and quartets all bound according to our calculations (see below). The interaction of the four quartet pairs of the same symmetry leads to 8 (Σ^- , Π , Δ , and Φ) quartets; including the four doublets 12 MRCI+Q PECs have been constructed, all bound with respect to the first channel $\text{Co}(a^4F) + \text{H}^-$; see Fig. 4. At the MRCI+Q level 7 anionic states are stable to electron detachment with respect to the $X^3\Phi$ state of CoH , by 0.70($X^4\Phi$), 0.46 ($I^4\Sigma^-$), 0.43 ($I^4\Pi$), 0.28 ($I^2\Delta$), 0.24 ($I^4\Delta$), 0.24 ($I^2\Phi$) and 0.11 ($I^2\Pi$) eV. The ground state of CoH^- is definitely of $^4\Phi$ symmetry.

1. $X^4\Phi$, $I^4\Sigma^-$, $I^4\Pi$, $I^4\Delta$

The above first four quartets of CoH^- can be thought of as the result of an electron attachment to the σ -frame of the $X^3\Phi$, $C^3\Sigma^-$, $B^3\Pi$, and $A^3\Delta$ states of CoH . As was already mentioned they all correlate diabatically to $\text{Co}^-(^3F) + \text{H}$, hence the negative charge on the *in situ* Co is close to one (see below). For the four quartets originating from the first channel, $\text{Co}(a^4F) + \text{H}^-(^1S)$, a slight interaction starts at 4 \AA , whereat a charge transfer of 0.1 e^- is observed from H^- to Co. At 3 \AA this amounts to 0.25 e^- while it is double as much at $r_e = 2.5$ \AA . From that point on the transfer increases steadily until it rests at equilibrium almost entirely on the cobalt atom ($\sim 0.9 e^-$), see Table VII. Most of the negative charge from H^- is directed to the $4p_z$ orbital of Co.

The first two dominant MRCI configurations and Mulliken atomic distributions of the $X^4\Phi$ state of CoH^- are

$$|X^4\Phi\rangle_{B1} \approx 0.58|1\sigma^22\sigma^23\sigma^11\pi_x^21\pi_y^11\delta_+^21\delta_-^1\rangle \\ - 0.58|1\sigma^22\sigma^23\sigma^11\pi_x^11\pi_y^21\delta_+^11\delta_-^2\rangle \\ 4s^{1.53}4p_z^{0.68}3d_z^2^{1.59}3d_{x^2}^{1.50}3d_{y^2}^{1.50}3d_{x^2-y^2}^{1.50}3d_{xy}^{1.50}/1s^{1.10}.$$

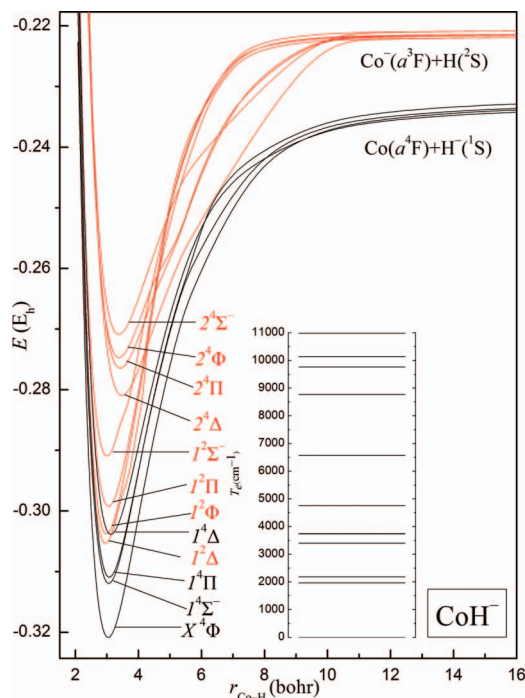


FIG. 4. MRCI+Q/A5 ζ PECs and energy level diagram (inset) of 12 states, 8 quartets, and 4 doublets of CoH $^-$.

The bonding interaction is represented by the 1σ orbital $1\sigma \approx (0.40)4s + (0.30)3d_{z^2} + (0.76)1s$ whereas the 2σ and 3σ orbitals are $4s3d_{z^2}$ and $4s3d_{z^2}4p_z$, hybrids, located entirely on the Co atom, their composition being $2\sigma \approx (0.64)4s - (0.71)3d_{z^2}$ and $3\sigma \approx (0.36)4s + (0.58)3d_{z^2} - (0.51)4p_z$. The *in situ* Co bears a Mulliken charge of $\sim 0.9 e^-$, entirely shared between the $4s$ and $4p_z$ orbitals.

The $X^4\Phi$ state has been also calculated by the coupled-cluster method including relativistic and subvalence core effects; see Table VI. Scalar relativity reduces the binding energy and bond distance by 2 (MRCI) to 3 (RCCSD(T)) kcal/mol and 0.008 to 0.004 Å. The MRCI+DKH2 (C-RCCSD(T)+DKH2) binding energy is $D_0 = 45.6$ (45.0) kcal/mol, both numbers in accord with the experimental value $D_0 = 43.1 \pm 1.2$ kcal/mol (see Sec. I). The experimental

bond length $r_0 = 1.67 \pm 0.03$ Å (Ref. 8) is considerably longer than that of the MRCI+DKH2+Q, $r_e = 1.600$ Å. Employing the corresponding calculated $\alpha_e = 0.282$ cm $^{-1}$ parameter in the formula $B_0 = B_e - \alpha_e/2$, we obtain $r_0 = 1.618$ Å, now in affordable agreement with experiment. The multireference (or coupled-cluster) calculated ω_e frequency cannot be compared readily with experiment due to the large error bars of the latter, ± 150 cm $^{-1}$ (Ref. 8). One more experimental datum is known for CoH $^-$: its ionization energy (or the EA of CoH), whence the dissociation energy of CoH $^-$ was obtained (*vide supra*). At the highest level EA (MRCI+DKH2+Q / C-RCCSD(T)+DKH2) = 0.731/0.674 in excellent agreement with the experimental value of 0.671 ± 0.01 eV.⁸ Finally the SO interaction splits the $X^4\Phi$ into four Ω components, 9/2, 7/2, 5/2, and 3/2 with $|A| = 174.0$ cm $^{-1}$, thus $T(\Delta\Omega = 1) = 3 \times A = 522$ cm $^{-1}$.

The leading MRCI CFs and atomic distributions of the $I^4\Sigma^-$, $I^4\Pi$, and $I^4\Delta$ states are given in Tables S8 and S9.⁵⁷ It suffices here to say that the bonding in the $I^4\Sigma^-$ and $I^4\Pi$ states is represented by the 1σ orbital, while the composition of the 2σ and 3σ orbitals is very similar to those of the $X^4\Phi$ state. In the $I^4\Delta$ state the 1σ is a pure $3d_{z^2}$ atomic function, the 2σ is the bonding orbital and the doubly occupied 3σ is a $4s3d_{z^2}4p_z$ hybrid on Co, its composition being similar to the 3σ of the $X^4\Phi$ state (*vide supra*). As in the $X^4\Phi$ the *in situ* Co atom in all three quartet states bears a negative charge close to one; see Table VII.

The MRCI+Q separation energies of the $I^4\Sigma^-$, $I^4\Pi$, and $I^4\Delta$ are $T_e = 1960, 2186,$ and 3736 cm $^{-1}$, respectively. The first order MRCI SO coupling constant is $|A| = 174.0$ ($X^4\Phi$), 179.5 ($I^4\Pi$), and 180.0 ($I^4\Delta$) cm $^{-1}$. Including the SO interaction the predicted energy separations between the lowest Ω component of each state become, $T_e = 1960 + 4.5 \times 174 = 2743$ ($I^4\Sigma^-$), $2186 + (4.5 \times 174 - 1.5 \times 179.5) = 2700$ ($I^4\Pi$), $3736 + (4.5 \times 174 - 3 \times 180) = 3979$ ($I^4\Delta$) cm $^{-1}$.

2. Second channel states, doublets, and quartets

As expected the four doublets which correlate adiabatically to $\text{Co}^-(a^3F) + \text{H}(^2S)$ are considerably lower in energy than the $2^4\Sigma^-$, $2^4\Pi$, $2^4\Delta$, and $2^4\Phi$ quartets; see Fig. 4. In the

TABLE VI. Total energies E (E_h), bond distances r_e (Å), dissociation energies D_e (kcal mol $^{-1}$), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm $^{-1}$), and rotational-vibrational coupling constants α_e (cm $^{-1}$), of the $X^4\Phi$ of CoH $^-$ at various levels of theory.

Method ^a	-E	r_e	D_e^b/D_0	ω_e	$\omega_e x_e$	α_e
MRCI	1382.301 87	1.615	50.7/48.5	1507	35.0	0.263
MRCI+Q	1382.320 99	1.608		1534	35.3	0.266
MRCI+DKH2	1392.741 92	1.609	47.7/45.6	1503	38.0	0.283
MRCI+DKH2+Q	1392.761 08	1.600		1537	37.1	0.282
RCCSD(T)	1382.314 62	1.601	49.2/47.0	1522	34.0	0.230
RCCSD(T)+DKH2	1392.754 98	1.598	46.1/43.9	1528	35.7	0.230
C-RCCSD(T)	1382.792 98	1.587	50.7/48.5	1573	35.2	0.271
C-RCCSD(T)+DKH2	1393.233 74	1.583	47.2/45.0	1572	37.5	0.264
Expt.		1.67 ± 0.03^c	43.1 ± 1.2^d	1300 ± 150^c		

^aSee Table I for explanation of acronyms and symbols.

^bWith respect to the ground state atoms, $\text{Co}(a^4F) + \text{H}(^1S)$.

^cReference 8; photoelectron spectroscopy; r_0 value.

^d D_0 value; calculated through the formula $D_0(\text{CoH}^-) = D_0(\text{CoH}) + \text{EA}(\text{CoH}) - \text{EA}(\text{H})$.

TABLE VII. Total energies E (E_h), bond distances r_e (\AA), dissociation energies D_e (kcal mol^{-1}), harmonic frequencies and anharmonicity corrections ω_e , $\omega_e x_e$ (cm^{-1}), rotational–vibrational coupling constants α_e (cm^{-1}), Mulliken charges on Co, q_{Co} , and energy separations, T_e (cm^{-1}) for 12 states of CoH^- at the MRCI+Q/A5 ζ level of theory.

State ^a	$-E$	r_e	D_e^b	ω_e	$\omega_e x_e$	α_e	q_{Co}	T_e
$X^4\Phi$ (a^4F)	1382.32099	1.608	50.7	1534	35.3	0.266	-0.88	0.0
$1^4\Sigma^-$ (a^4F)	1382.31206	1.617	46.2	1493	35.8	0.266	-0.86	1960
$1^4\Pi$ (a^4F)	1382.31103	1.627	44.0	1484	37.1	0.266	-0.83	2186
$1^2\Delta$ (Co^- ; 3F)	1382.30550	1.563	54.7	1602	35.3	0.253	-1.09	3399
$1^4\Delta$ (a^4F)	1382.30397	1.652	36.6	1395	35.3	0.256	-0.77	3736
$1^2\Phi$ (Co^- ; 3F)	1382.30394	1.579	54.1	1584	35.6	0.299	-1.02	3742
$1^2\Pi$ (Co^- ; 3F)	1382.29935	1.616	50.8	1505	34.5	0.265	-1.02	4749
$1^2\Sigma^-$ (Co^- ; 3F)	1382.29105	1.586	47.2	1528	36.7	0.255	-1.01	6571
$2^4\Delta$ (Co^- ; 3F)	1382.28104	1.838	44.0	1107	34.0	0.263	-0.68	8769
$2^4\Pi$ (Co^- ; 3F)	1382.27649	1.808	38.8	1108	34.8	0.267	-0.70	9765
$2^4\Phi$ (Co^- ; 3F)	1382.27479	1.789	38.0	1130	39.1	0.300	-0.70	10 141
$2^4\Sigma^-$ (Co^- ; 3F)	1382.27095	1.786	35.3	1142	37.5	0.265	-0.70	10 982

^aValues in parentheses after the molecular term symbol denote the end term of Co or Co^- .

^bAdiabatic D_e values at the MRCI/A5 ζ level.

latter the total negative charge on the Co atom is 0.7, increasing to 1.0 in the doublets. In addition the bond distance of all doublets is by ~ 0.2 \AA shorter than that of the higher quarters. Three out of the four doublets ($1^2\Delta$, $1^2\Phi$, $1^2\Pi$) are stable with respect to the $X^3\Phi$ state of CoH, whereas all higher quarters are unstable to electron detachment.

MRCI results, leading configurations, and atomic populations for all 12 states of CoH^- are given in Tables S7, S8, and S9.⁵⁷

IV. SUMMARY AND REMARKS

The diatomic hydride CoH and its ions CoH^\pm have been studied by all electron high level variational multireference (MRCI) and single reference coupled-cluster (RCCSD(T)) methods, in conjunction with correlation-consistent basis sets of quintuple cardinality. Our motivation was the inherent interest on the 3d–MH hydrides as prototype diatomic molecules, the scarcity of experimental data on the CoH^\pm species, and, surprisingly, the lack of a systematic and thorough all electron first principles calculations, particularly for CoH. This should be related to the fact that although the H atom is computationally an ideal “ligand,” recall that its first excited state is 10.2 eV high, CoH is a very demanding and capricious system burdened with all complications of 3d transition metal containing molecules. For 27 (CoH), 24 (CoH^+), and 12 (CoH^-) bound states we report MRCI+Q potential energy curves, common spectroscopic parameters, dissociation energies, dipole moments (CoH), separation energies, and SO coupling constants for the ground and low-lying states. Scalar relativistic corrections and core subvalence ($3s^23p^6$) correlation effects have been also applied to the ground states of CoH, and CoH^\pm . Our findings are outlined below.

1. Almost all our numerical results are in fairly good agreement to existing experimental data. For instance, the binding energies of the ground states of CoH, CoH^+ , and CoH^- are (experimental values in parentheses), $D_0^0 = 46.4 \pm 0.5(45.0 \pm 1.2)$, $49.6(47 \pm 2)$, and $45.6(43.1 \pm 1.2)$ kcal/mol, respectively. Observe that the

calculated dissociation energies are consistently about 1 kcal/mol higher than the experimental D_0^0 values. There is one serious discrepancy, however, between experiment and theory concerning the electric dipole moments of the $X^3\Phi_4$ and $2(A')^3\Phi_4$ states of CoH. According to Steimle and co-workers²¹ $\mu = 1.88 \pm 0.08$ and 0.01 ± 0.08 D, as contrasted to the calculated finite-field values of 2.6 and 0.43 D for the $X^3\Phi$ and $A'^3\Phi$ states, respectively. Previous *ab initio* calculations give even higher μ values for the $X^3\Phi$ state of CoH. Since all our calculations even those of a much larger extent (MRCI–L for the ground state) gave numbers ~ 0.6 ($X^3\Phi$) and ~ 0.4 D ($A'^3\Phi$) higher than experiment, we believe that theoretically, at least, the dipole moment is established to be higher than the experimental measurement. We believe that this disagreement will trigger further experimental investigation.

2. The ground states of CoH, CoH^+ , and CoH^- are of $^3\Phi_4$, $^4\Phi$, and $^4\Phi$ symmetries, respectively. For the CoH^+ a $^4\Sigma^-$ competes strongly with being the ground state located 395 cm^{-1} higher. The SO interaction, however, lowers an Ω component of the $^4\Phi$ by as much as 809 cm^{-1} , therefore should the SO coupling constant A be negative, the $^4\Phi_{9/2}$ state is the ground state of CoH^+ ; otherwise the ground state of CoH^+ is $^4\Phi_{3/2}$ (regular).
3. In all states of CoH a Co–to–H Mulliken charge transfer of $0.2\text{--}0.3 e^-$ is calculated. In CoH^+ the Co atom retains its $+1$ charge from infinity to equilibrium ($\text{Co}^+ \text{--} \text{H}$), whereas in CoH^- $0.7\text{--}0.9 e^-$ are transferred from $\text{H}^- \text{--} \text{to} \text{--} \text{Co}$ through avoided crossings ($\text{Co}^- \text{--} \text{H}$).
4. Neither the ground state configuration of Co ($4s^23d^7$; a^4F) nor of $\text{Co}^+(3d^8$; a^3F) are conducive to bond formation with $\text{H}(^2S)$. The $3d^74s^2$ (Co) or $3d^8$ (Co^+) electron configuration precludes any strong interaction other than that of a van–der–Waals nature. It seems that a cobalt configuration of $3d^74s^1$ is a *conditio sine qua non* for obtaining strongly bound states. This is verified from the Mulliken populations of the ground and excited states of both CoH and CoH^+ whose

equilibrium 4s orbital population has an occupation close to one. Therefore strong (Co, Co⁺) + H attractive interactions are related to higher states of Co and Co⁺. This obviously creates technical as well as interpretational problems, a common situation, surely, in 3d-MX diatomics. In CoH⁻ bonding is related to the second channel, Co⁻(³F; 4s²3d⁸) + H(²S), experimentally (theoretically) 0.10 (0.42) eV above the ground state end fragments Co (⁴F) + H⁻(¹S).

- In general core subvalence effects (3s²3p⁶) are of minor importance, scalar relativistic effects, however, are significant in consistently reducing binding energies by a few percent. This reduction is also observed in bond distances the values of which are driven away from corresponding experimental when relativity enters. The fact that at higher levels of calculation, including relativistic corrections, smaller r_e 's are obtained, is certainly a remarkable discrepancy.

We would like to believe that the present work is a useful contribution to the theoretical literature of the 3d-MH diatomic hydrides, and that it would further instigate experimental and theoretical work on this interesting and prototypic class of molecules.

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