J. Phys. Chem. A **2007,** *111,* 371−374

A Theoretical Study of Calcium Monohydride, CaH: Low-Lying States and Their Permanent Electric Dipole Moments

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Received: July 24, 2006; In Final Form: October 23, 2006

Potential energy curves, energy parameters, and spectroscopic values for the X $^2\Sigma^+$, A $^2\Pi$, B $^2\Sigma^+$, a $^4\Pi$, and b $^4\Sigma^+$ states of CaH have been calculated using the multireference configuration interaction and coupled cluster levels of theory, while employing quantitative basis sets (of augmented quintuple-ζ quality) and taking also into account core/valence correlation and one-electron relativistic effects. For the ground (X $^2\Sigma^+$) and the first two following excited states (A $^2\Pi$, B $^2\Sigma^+$) of CaH, the permanent electric dipole moments have been calculated. Our best *finite field* dipole moment of the A $^2\Pi$ state of 2.425 D ($v = 0$) is in very good agreement with the experimental literature value of 2.372(12) D. However, a discrepancy is observed in the dipole moment of the X $^2\Sigma^+$ state. Our most extensive calculation gives $\mu = 2.623$ D ($v = 0$), which is considerably smaller than the experimental value of $\mu = 2.94(16)$ D ($v = 0$). Small van der Waals minima were found for both "repulsive" quartet states. Spectroscopic constants and energy parameters for all states are in remarkable agreement with available experimental values.

1. Introduction

About a century has passed since the first observation of calcium monohydride in the Sun and in the laboratory by Olmsted and Eagle, respectively.[1,2] Ever since, a large part of experimental work has been devoted to its spectroscopy.[3] However, the permanent electric dipole moments μ of the ground $^2\Sigma^+$ and the first excited $^2\Pi$ state of CaH were measured for the first time only very recently.[4] Employing optical Stark spectroscopy experiments, Steimle et al. found values of 2.94(16) and 2.372(12) D for the X $^2\Sigma^+$ ($v = 0$) and A $^2\Pi$ ($v = 0$) states, respectively.[4] When compared with previous theoretical μ values,[5−10] a discrepancy of at least 0.4 D was found for the ground state, whereas a much smaller difference was noted for the A $^2\Pi$ state.

The reliable theoretical determination of permanent electric dipole moments is not a trivial task. In general, electric dipole moments can be extracted theoretically by two means, either as an expectation value of an exact or approximate wavefunction Φ,

$$\vec{\mu} = \langle \Phi | \hat{\vec{\mu}} | \Phi \rangle \tag{1}$$

or as the gradient of the total energy E of the system with respect to an external field ϵ, that is,

$$\vec{\mu} = \nabla_{\epsilon} E \tag{2}$$

where $\nabla_{\epsilon} = (\partial/\partial\epsilon_x, \partial/\partial\epsilon_y, \partial/\partial\epsilon_z)$.

In the case of a diatomic molecule lying along the z-axis, the dipole moment can be calculated using finite energy differences:

$$\mu_z = \lim_{\delta\epsilon_z \to 0} \frac{\delta E}{\delta \epsilon_z} \tag{3}$$

where δE is the energy difference before and after the application of an external electric field ($\delta\epsilon_z$) along the z-axis.

As we have previously shown,[11] eq 3 is recommended in general in order to extract reliable theoretical μ values, since the expectation value approach (eq 1) may provide inaccurate values if the quality of the wavefunction is not superb.

Stimulated by the experimental study of Steimle et al., we intend to calculate at a very high level of theory dipole moments for the two lowest states of CaH that have been studied by Steimle et al.[4] Furthermore, we also present full potential energy curves for these states, as well as for the three excited states that follow in ascending energy order.

2. Technical Details

We have employed the multireference configuration interaction (MRCI) and the (restricted) coupled cluster method including single and double excitations, along with a noniterative estimate of the connected triple excitations, based on a restricted Hartree−Fock reference wavefunction, RHF−RCCSD(T) method.[12] For Ca, the valence correlation-consistent basis set of quintuple-ζ quality (cc-pV5Z) published by Koput and Peterson was used.[13] The effect of the $3s^2 3p^6$ first core shell of Ca was taken into account with the use of the "Core" (cc-pCV5Z) and "weighted Core" (cc-pwCV5Z) basis sets.[14] For H, a similar quality basis set was used, augmented with diffuse functions (aug-cc-pV5Z)[15] due to the expected negatively charged character of H. In certain cases, the effect of a second diffuse shell on H was examined (d-aug-cc-pV5Z).[16] The largest basis set used in the present work, d-aug-cc-pCV5Z=$(26s18p12d6f4g2h/_{\mathrm{Ca}}10s6p5d4f3g/_{\mathrm{H}}) \rightarrow [12s10p9d6f4g2h/_{\mathrm{Ca}}\ 7s6p5d4f3g/_{\mathrm{H}}]$ numbers 292 generally contracted spherical Gaussian functions. One-electron second-order Douglas−Kroll−Hess (DKH) relativistic

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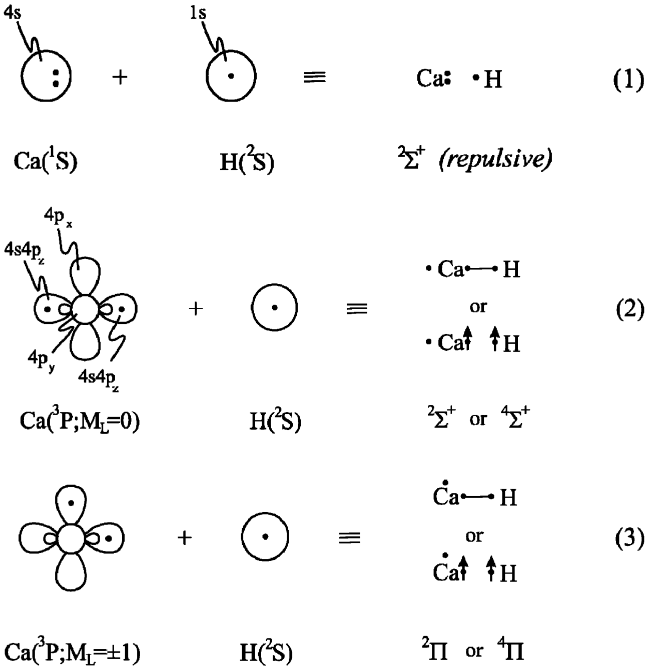
10.1021/jp064705k CCC: $37.00

effects were taken into account using completely uncontracted versions of the aforementioned basis sets. Dipole moments were calculated either as expectation values (MRCI level) or with the finite field method [MRCI and RCCSD(T)], utilizing a two point finite difference formula with respective field strengths of +0.00001 and −0.00001 au. All calculations were performed with the molpro 2002.6 software package.[17]

3. Results and Discussion

The interaction of Ca(^{1}S, ^{3}P) + H(^{2}S) is expected to lead to two $^2\Sigma^+$, one $^2\Pi$, one $^4\Sigma^+$, and one $^4\Pi$ CaH state according to the following valence-bond-Lewis (vbL) diagrams:



Reaction 1 shows that when the ground-state fragments Ca(^{1}S) + H(^{2}S) interact with each other, a repulsive (or van der Waals bound) $^2\Sigma^+$ state is formed. Therefore, the X $^2\Sigma^+$ state of CaH actually traces its lineage to the *excited* Ca(^{3}P; $4s^14p^1$) + H(^{2}S) dissociation limit, according to reaction 2. Within the "clamped nuclei" approximation, we expect to observe an avoided crossing between these two $^2\Sigma^+$ states (*vide infra*). The participation of the ^{3}P state of Ca in the X $^2\Sigma^+$ and A $^2\Pi$ states of CaH points out the need for a proper description of the Ca $^3P \leftarrow {}^1S$ energy gap.

Table 1 lists calculated energies for the ground and first excited state of Ca, ^{1}S and ^{3}P, respectively, as well as their energy difference. We note that the role of $3s^23p^6$ "semi-core" electrons is crucial in obtaining a satisfactory value for the $^3P \leftarrow {}^1S$ energy separation. Hardly any difference can be found between the results of two core/valence basis sets. In either C-MRCI (i.e., MRCI with $3s^23p^6$ core/valence correlation included), C-MRCI+Q or C-RCCSD(T) levels of theory, the difference between the theoretically predicted and the experimental energy gap is less than 250 cm^{-1}.

Calculated data for the bound low-lying doublet states of CaH (X $^2\Sigma^+$, A $^2\Pi$, and B $^2\Sigma^+$) are collected in Tables 2, 3, and 4, respectively, while Figure 1 displays the low-lying state manifold of CaH calculated at the C-MRCI+Q/(cc-pCV5Z/$_{\mathrm{Ca}}$ aug-cc-pV5Z/$_{\mathrm{H}}$) level of theory. At about 7 bohr, we note the aforementioned avoided crossing between the X $^2\Sigma^+$ and B $^2\Sigma^+$ states, which is responsible for the electronic character change of the *in situ* Ca from ^{1}S to ^{3}P in the X $^2\Sigma^+$ state.

TABLE 1: Total Energies (E_h) of the ^{1}S and ^{3}P States of Ca and Their Separation T_e (cm^{-1}) at the MRCI and RCCSD(T) Levels of Theory

method/basis set	Ca(^{1}S)	Ca(^{3}P)	T_e
MRCI/cc-pV5Z	−676.787 104	−676.725 306	13 563.0
C-MRCI/cc-pCV5Z	−677.078 644	−677.009 655	15 141.3
C-MRCI/cc-pwCV5Z	−677.075 701	−677.006 648	15 155.3
MRCI+Q/cc-pV5Z	−676.787 10	−676.725 31	13 563
C-MRCI+Q/cc-pCV5Z	−677.097 83	−677.028 86	15 136
C-MRCI+Q/cc-pwCV5Z	−677.094 76	−677.025 73	15 150
RCCSD/cc-pV5Z	−676.787 102	−676.725 484	13 523.6
C-RCCSD(T)/cc-pCV5Z	−677.102 183	−677.033 719	15 026.1
C-RCCSD(T)/cc-pwCV5Z	−677.099 033	−677.030 481	15 045.4
DKH-C-RCCSD(T)/cc-pCV5Z[a]	−679.972 822	−679.903 311	15 255.9
experiment[b]			15 276.238

[a] Uncontracted basis used. [b] M_J-averaged value, ref 18.

TABLE 2: Total Energies E (E_h), Binding Energies D_e (kcal/mol), Bond Lengths r_e (Å), and Dipole Moments (D) Calculated as Expectation Values, $\langle\mu\rangle$, or by the Finite Field Method, μ_{FF}, for the X $^2\Sigma^+$ State of CaH at Various Levels of Theory[a]

method	E	D_e	r_e	$\langle\mu\rangle$	μ_{FF}
		Basis cc-pV5Z/$_{\mathrm{Ca}}$aug-cc-pV5Z/$_{\mathrm{H}}$			
MRCI	−677.354 911	42.6	2.0511	2.384	2.361
MRCI+Q	−677.355 11	42.7	2.051		2.37
RCCSD(T)	−677.354 567	42.3	2.0546		2.354
		Basis cc-pCV5Z/$_{\mathrm{Ca}}$aug-cc-pV5Z/$_{\mathrm{H}}$			
C-MRCI	−677.643 111	40.5	2.0100	2.023	2.463
C-MRCI+Q	−677.663 57	41.3	2.004		2.50
C-RCCSD(T)	−677.668 248	41.5	2.0026		2.520
		Basis cc-pCV5Z/$_{\mathrm{Ca}}$d-aug-cc-pV5Z/$_{\mathrm{H}}$			
C-RCCSD(T)	−677.668 274	41.5	2.0026		2.523
		Basis cc-pwCV5Z/$_{\mathrm{Ca}}$aug-cc-pV5Z/$_{\mathrm{H}}$			
C-RCCSD(T)	−677.665 094	41.5	2.0023		2.522
		Basis cc-pCV5Z/$_{\mathrm{Ca}}$aug-cc-pV5Z/$_{\mathrm{H}}$ (Uncontracted)			
DKH-C-RCCSD(T)	−680.537 807	40.8	2.0035		2.538
CISD[b]		39.2	1.99	2.463	
ROMP2[c]					2.584
DFT[d]					2.68
RCCSD(T)[e]		40.9	2.008		2.33
DFT[f]			1.996		
FCI+CPP[g]		38.3	1.981		
experiment		≤41.1,[h] 53.5[i]	2.0025[h]	2.94(16)[j]	

[a] Experimental results are shown for comparison. [b] Reference 5. [c] Restricted open-shell second-order Møller−Plesset perturbation theory at the experimental bond length, ref 6. [d] Calculated at the experimental r_e, ref 7. [e] Reference 8. [f] Density functional theory at the B3LYP/6-31++G** level, ω_e = 1283 cm^{-1}, ref 9 [g] Full CI+Core Polarization Potential, ref 10. [h] Reference 19. [i] Curve fitting to molecular constants using the Rydberg−Klein−Rees−Vanderslice potential, ref 20. [j] Optical Stark spectroscopy, ref 4.

When $3s^23p^6$ core/valence effects are neglected, the dipole moment of the X $^2\Sigma^+$ state of CaH is found to be about 2.35−2.37 D, depending on the level of theory used (Table 2). Due to the small number of "active" electrons, the MRCI wavefunction recovers practically all the valence electron correlation leading to practically no difference between the expectation value $\langle\mu\rangle$ and the finite field value μ_{FF} of the dipole moment at this level of theory. However, $3s^23p^6$ core/valence correlation needs to be included to bring the rather long (by ~0.05 Å) bond length in accordance with the experimental value of 2.0025 Å.[19] As shown in Table 2, inclusion of these eight electrons in the correlation treatment brings the calculated bond length and binding energy of CaH to practical agreement with the experiment. We consider our best D_e and r_e values for the ground

TABLE 3: Total Energies E (E_h), Binding Energies D_e (kcal/mol), Bond Lengths r_e (Å), A $^2\Pi \leftarrow$ X $^2\Sigma^+$ Transition Energies T_e (cm^{-1}), and Dipole Moments (D) Calculated as Expectation Values, $\langle\mu\rangle$, or by the Finite Field Method, μ_{FF}, for the A $^2\Pi$ State of CaH at Various Levels of Theory[a]

method	E	D_e	r_e	T_e	$\langle\mu\rangle$	μ_{FF}
	Basis cc-pV5Z/$_{\text{Ca}}$aug-cc-pV5Z/$_{\text{H}}$					
MRCI	−677.291 611	41.6	2.0131	13 892.7	2.867	2.903
MRCI+Q	−677.292 23	41.9	2.014	13 799		2.94
RCCSD(T)	−677.291 151	41.2	2.0150	13 918.2		2.866
	Basis cc-pCV5Z/$_{\text{Ca}}$aug-cc-pV5Z/$_{\text{H}}$					
C-MRCI	−677.576 286	41.5	1.9761	14 666.4	2.441	2.406
C-MRCI+Q	−677.598 08	43.2	1.972	14 372		2.41
C-RCCSD(T)	−677.603 026	43.5	1.9742	14 314.6		2.376
	Basis cc-pCV5Z/$_{\text{Ca}}$d-aug-cc-pV5Z/$_{\text{H}}$					
C-RCCSD(T)	−677.603 061	43.5	1.9742	14 312.6		2.368
	Basis cc-pwCV5Z/$_{\text{Ca}}$aug-cc-pV5Z/$_{\text{H}}$					
C-RCCSD(T)	−677.599 846	43.5	1.9740	14 320.3		2.370
	Basis cc-pCV5Z/$_{\text{Ca}}$aug-cc-pV5Z/$_{\text{H}}$ (Uncontracted)					
DKH-C-RCCSD(T)	−680.471 724	42.9	1.9716	14 503.5		2.380
CISD[b]		41.1	1.97	14 524	2.359	
FCI+CPP[c]			1.96	14 132		
experiment			1.9740[d]	14 413[d]		2.372(12)[e]

[a] Experimental results are shown for comparison. [b] Reference 5. [c] Full CI+Core Polarization Potential, ref 10. [d] Reference 19. [e] Optical Stark spectroscopy, ref 4.

TABLE 4: Total Energies E (E_h), Binding Energies D_e (kcal/mol), Bond Lengths r_e (Å), B $^2\Sigma^+ \leftarrow$ X $^2\Sigma^+$ Transition Energies T_e (cm^{-1}), and Dipole Moments (D) Calculated as Expectation Values, $\langle\mu\rangle$, or by the Finite Field Method, μ_{FF}, for the B $^2\Sigma^+$ State of CaH, Using the cc-pCV5Z$_{\text{Ca}}$/aug-cc-pV5Z$_{\text{H}}$ Basis Set[a]

method	E	D_e	r_e	T_e	$\langle\mu\rangle$	μ_{FF}
C-MRCI	−677.572 093	41.9	1.9745	15 586.6	2.329	2.871
C-MRCI+Q	−677.593 04	42.3	1.970	15 479		2.83
experiment[b]			1.9744	15 762		

[a] Experimental results are shown for comparison. [b] Reference 19.

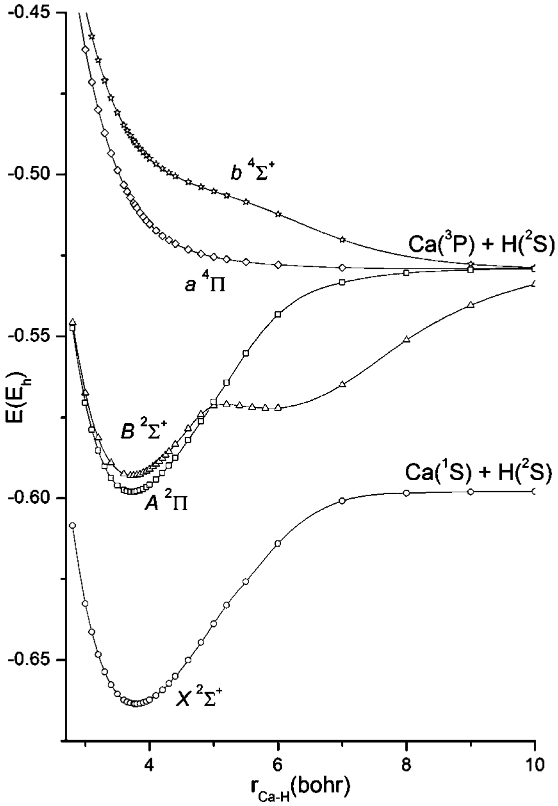


Figure 1. Potential energy curves of the X $^2\Sigma^+$, A $^2\Pi$, B $^2\Sigma^+$, a $^4\Pi$, and b $^4\Sigma^+$ states of CaH at the C-MRCI+Q/(cc-pCV5Z/$_{\text{Ca}}$ aug-cc-pV5Z/$_{\text{H}}$) level of theory.

state of calcium monohydride to be 40.8 kcal/mol and 2.0035 Å at the DKH-C-RCCSD(T)/(cc-pCV5Z/$_{\text{Ca}}$ aug-cc-pV5Z/$_{\text{H}}$) level of theory, with corresponding experimental values of 41.1 kcal/mol (upper limit) and 2.0025 Å.[19] The D_e value of 53.5 kcal/mol obtained by Partal Ureña et al.[20] is certainly not realistic. Numerical solution of the rovibrational Schrödinger equation using the calculated potential energy curve at the C-MRCI+Q/(cc-pCV5Z/$_{\text{Ca}}$ aug-cc-pV5Z/$_{\text{H}}$) level of theory gave harmonic and anharmonic frequencies $\omega_e = 1302.9$ cm^{-1} and $\omega_e x_e = 18.5$ cm^{-1}, which agree with the experimental values of 1298.34 and 19.10 cm^{-1}, respectively.[19] Due to the increased number of "active" electrons in the correlation treatment, the C-MRCI expectation value of the dipole moment is about 0.4 D smaller than the finite field value, an effect already noted before.[11] The "best" calculated nonrelativistic finite field value of the dipole moment [C-RCCSD(T)/(cc-pCV5Z/$_{\text{Ca}}$ d-aug-cc-pV5Z/$_{\text{H}}$)] is 2.523 D, which is still significantly smaller than the experimental value of 2.94 ± 0.16 D obtained by Steimle and co-workers.[4] Since the experimental μ value refers to the $v = 0$ vibrational level, we calculated the dipole moment at the $r_0 = 2.0250$ Å distance extracted from the numerical solution of the rovibrational Schrödinger equation (*vide supra*). The corresponding dipole moment was about 0.08 D larger, giving 2.605 D at the RCCSD(T) level of theory. DKH relativistic effects contribute another +0.018 D to the dipole moment bringing it to an ultimate value of 2.623 D. Therefore, a discrepancy of about 0.32 D still exists compared with experiment. We should note however that this discrepancy is not very large; indeed our value is roughly within the experimental value at a 2σ standard deviation limit.

Following the same path in examining the A $^2\Pi$ state (Table 3), we note that our largest calculation [DKH-RCCSD(T)/(cc-pCV5Z/$_{\text{Ca}}$ aug-cc-pV5Z/$_{\text{H}}$) level] gives r_e and T_e values that are again in excellent agreement with experiment,[19] 1.9716 Å and 14 503.5 cm^{-1} vs 1.9740 Å and 14 413 cm^{-1} respectively. Similar agreement is observed for the C-MRCI+Q harmonic and anharmonic frequencies of 1347.8 and 19.5 cm^{-1} respectively, compared with experimental values of 1333 and 20 cm^{-1}.[19] Here, however, there is accordance of the calculated (finite field) dipole moment with the experimental value of Steimle and co-workers,[4] 2.368 vs 2.372 ± 0.012 D. The agreement stands even after correcting for the $v = 0$ vibrational level; a calculation at the $r_0 = 1.9940$ Å gives ultimately $\mu(v = 0) = 2.425$ D including relativistic corrections.

Calculation of the B $^2\Sigma^+$ potential energy curve presented many convergence problems, probably due to consecutive avoided crossings as shown in Figure 1. The 3d orbitals of Ca had to be included in the CAS active space in order for the calculations to converge properly. Starting from the Ca(^{3}P) + H(^{2}S) channel and approaching toward equilibrium, the first avoided crossing appears at around 7 bohr with the repulsive $^2\Sigma^+$ state emerging from the ground state Ca(^{1}S) + H(^{2}S) reactants. A second avoided crossing appears near 5 bohr from an incoming $^2\Sigma^+$ state, possibly stemming from the Ca(^{3}D; 4s^1-3d^1) + H(^{2}S) reactants, ~20 350 cm^{-1} above the ground state dissociation channel.[18] Due to the intrinsic nature of this excited state, it was possible to use only a multistate multireference variational method like the MRCI method. As shown in Table 4, the theoretical predictions are quite accurate as compared with experimental values (where available). In particular, we note the mere <300 cm^{-1} difference from the B $^2\Sigma^+ \leftarrow$ X $^2\Sigma^+$ experimental transition energy. The dipole moment at the C-MRCI+Q level of theory was found to be $\mu_{FF} = 2.832$ D.

Finally, the two "repulsive" quartets exhibit weak van der Waals (vdW) minima at large internuclear distances. From reactions 2 and 3, we would expect the $^4\Pi$ state to be less repulsive than the $^4\Sigma^+$ state, and indeed calculations at the valence MRCI+Q/(cc-pV5Z$_{Ca}$/aug-cc-pV5Z$_H$) level of theory confirm this hypothesis. Predicted ΔE_{vdW} and r_{vdW} values for the a $^4\Pi$ and b $^4\Sigma^+$ states are 27.4 cm^{-1} at 4.72 Å and 3.0 cm^{-1} at 7.7 Å, respectively.

4. Summary and Concluding Remarks

The discrepancy of the experimentally determined electric dipole moment of the ground state CaH with theoretical values has motivated this work. Even though total agreement was achieved with the (more accurately determined) experimental dipole moment of the excited A $^2\Pi$ state, a discrepancy of about 0.32 D still remains for the X $^2\Sigma^+$ state. In view of the otherwise complete agreement with the experimental D_e, r_e, and T_e values for these two states, and μ for the A $^2\Pi$ state, our inability to converge to the experimental value of the dipole moment of the X $^2\Sigma^+$ state (assuming that the experimental number is accurate enough) could be traced perhaps to the ionic character of the CaH X state. Our MRCI (and CASSCF) Mulliken distributions point to a charge transfer of 0.40 e$^-$ from Ca to H. This strong ionic character around equilibrium can be attributed to an interaction of the ionic Ca$^+$(4s^1; ^{2}S) + H$^-$(1s^2; ^{1}S) $^2\Sigma^+$ state with the X $^2\Sigma^+$ and B $^2\Sigma^+$ states, asymptotically located 6.11 (Ca $\rightarrow$ Ca$^+$ + e$^-$) $-$ 0.75 (H + e$^-$ $\rightarrow$ H$^-$) = 6.86 eV above Ca(^{1}S) + H(^{2}S). If our C-MRCI calculations and more so the coupled cluster ones cannot represent faithfully these interactions, the ionic character of the X $^2\Sigma^+$ state is underestimated, and this is reflected in the calculated dipole moment. We also feel that, perhaps, a more fastidious re-examination of the experimental data of the electric dipole moment of CaH(X $^2\Sigma^+$) is needed in order to resolve this interesting discrepancy between theory and experiment.

Finally, the B $^2\Sigma^+$ state and the van der Waals interactions in the a $^4\Pi$ and b $^4\Sigma^+$ states of CaH were also examined and calculated at a fairly high level of theory.

Note added in proof. While our manuscript was under review, F. Holka and M. Urban [*Chem. Phys. Lett.* **2006**, *426*, 252] published a relevant theoretical study on the dipole moment and molecular properties of the CaH X state employing coupled cluster methods and extensive basis sets. They also found a similar discrepancy with experiment, their best result for the dipole moment being 2.617 D.

Acknowledgment. The authors would like to thank Professor Kirk A. Peterson for communicating the core/valence basis sets of Ca prior to publication. The project was cofunded by the European Social Fund and National Resources − (EPEAEK II) PYTHAGORAS (Grant No. 70/3/7373). One of us (A.M.) expresses his gratitude to the National and Kapodistrian University of Athens for financial support through its Special Account 70/4/7565 for Basic Research.

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