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ARTICLE

All-electron relativistic spin-orbit multireference computation to elucidate the ground state of CeH

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The all-electron relativistic spin-orbit multiconfiguration/multireference computations with the Sapporo basis sets were carried out to elucidate characters of the low-lying quasi-degenerate electronic states for the CeH diatomic molecule. The present computations predict the ground state of CeH to be a pure quartet state of $4f^1 5d^1 (5d_\sigma\text{-}H_{1s})^2 6s^1$ configuration (Ω = 3.5). The first excited state (Ω = 2.5) shows a doublet dominant of $4f^1 (5d_\sigma\text{-}H_{1s})^2 6s^2$ configuration in a short bond length while it changes to a quartet dominant in a long bond length. The Ce-H stretching fundamental frequency was calculated to be 1345 cm^{-1} in the ground state, which is in good agreement with the experimental value, 1271 cm^{-1}, measured by a matrix-isolation technique.

Introduction

The electronic structure of the lanthanide compounds has a complexity due to partially-filled 4f orbitals in a lanthanide atom with the low-lying nearly-degenerate electronic states, which requires a relativistic molecular theory including the spin-orbit coupling effects. Yabushita and coworkers[1] employed the relativistic effective core potential (RECP) approach[2] to investigate the low energy spin-orbit multiplet terms of the trivalent lanthanide cations, Ln^{3+}, including the spin-orbit coupling effect explicitly by the full-variational spin-orbit configuration interaction (SOCI) method. One of the authors (TT)[3] employed a state-averaged complete active space multiconfigurational self-consistent field (SA-CASSCF) method[4] with the RECP to discuss the electronic and geometric structures of a series of the lanthanide trihalides, LnX_3 (Ln = La–Lu; X = Cl, F), including the spin-orbit coupling effect explicitly. As an alternative to the RECP approach, the all-electron relativistic theory based on the two-component Douglas–Kroll–Hess (DKH) method has been developed.[5,6] Nakajima and Hirao proposed the higher-order DKH method by introducing the unitary operator of an exponential form.[7] Such a two-component relativistic approach requires a development of the all-electron basis set in which the parameters should be determined from the relativistic quantum-chemical calculations. Noro and coworkers have developed a family of the all-electron Sapporo basis sets systematically for all the elements in a periodic table.[8–10] Schoendorff and Wilson[11] employed the CASSCF and coupled-cluster methods with the Sapporo triple-zeta basis sets to investigate the spectroscopic constants of the ground and low-lying excited states of the lanthanide monofluorides, NdF and LuF. Armentrout and coworkers[12] examined the electronic structure, geometrical structure, and energetics of SmS^+ by *ab initio* electronic structure calculations using the all-electron cc-pV*x*Z-DK3 (*x* = D, T, Q) basis set[13], which was compared with the guided ion beam experiment.

The ground-state configuration of the Ce atom is $[Xe]4f^1 5d^1 6s^2$, while that of the Ce^+ ion is $[Xe]4f^1 5d^2$ with a slightly-higher excited-state configuration of $[Xe]4f^1 5d^1 6s^1$.[14] Recently, we[15] investigated the energy levels of the low-lying electronic states of Ce^+ and CeF by employing the SA-CASSCF and *n*-electron valence state 2nd-order multireference perturbation theory (NEVPT2)[16–18] with the Sapporo-DKH3-QZP-2012 and Sapporo-QZP-2012 basis sets. We calculated the energy levels of 70 quartet states originating from the $[Xe]4f^1 5d^2$ configuration (^{4}S, ^{4}P, ^{4}D×2, ^{4}F×2, ^{4}G×2, ^{4}H, and ^{4}I) and 35 quartet states originating from the $[Xe]4f^1 5d^1 6s^1$ configuration (^{4}P, ^{4}D, ^{4}F, ^{4}G, and ^{4}H) for Ce^+; considering a spin-multiplicity of quartet, the number of the independent electronic states increases with a factor of four (280 and 140, respectively), which can be used as the basis functions to represent the eigenstates including the spin-orbit coupling; we estimated the *J*-averaged values from the experimental data where *J* is the total angular momentum quantum number, and verified a good agreement between the experiment and calculation. This methodology was applied to CeF to evaluate the relative energies of the low-lying electronic states, the equilibrium bond length, and stretching frequency, which were consistent with the experimental values.[15]

The above procedure where (1) the energy calculation is performed for the spin-free states, (2) the spin-orbit coupling terms are calculated for the spin-free states, and (3) the spin-orbit coupling matrix is diagonalized to obtain the spin-orbit

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coupled states, is called two-step spin-orbit scheme. If the spin-orbit coupling is too relevant, not the two-step spin-orbit scheme but a full-relativistic calculation such as four components Dirac-Coulomb approach is considered to be required. Also, the use of the state-average approach seems problematic because the use of average orbitals instead of the orbitals optimized for each state introduces errors in energy differences between different states. However, the two-step spin-orbit scheme works very well in our previous calculations for the nearly degenerate electronic states of Ce^+, which shows a quantitative agreement with the experimental values.[15] This previous calculation also suggested a good performance of NEVPT2/SA-CASSCF method for the near-degenerate electronic states.

Hence, we turn to the lanthanide monohydride, CeH. The bonding nature in CeF is almost a pure ionic bond between Ce^+ and F^-, while the bond in CeH has a covalent nature between the Ce atomic orbital and H-1s orbital. Since the inner-shell 4f orbitals are contracted inside, the H-1s orbital should make a bond with the $5d_\sigma$ orbital of Ce. Dolg *et al.*[19] examined the bond length and vibrational frequency of CeH in the doublet state with a configuration of $4f^1$, using the *ab initio* configuration interaction with singles and doubles (CISD) method with the RECP. Willson and Andrews[20] performed a combined study of matrix-isolation spectroscopy and density functional theory (DFT) calculations on CeH where only the quartet state was examined. Actually, it is very difficult to determine the nature of the ground state of CeH by theoretical calculations without the spin-orbit coupling effect, because both the doublet and quartet states are good candidates of the lowest electronic state. In this study, we employ an all-electron *ab initio* spin-orbit multiconfigurational/mutireference approach with the Sapporo basis sets based on a two-component relativistic scheme to examine the character of the ground and low-lying excited states of CeH.

Computational details

We investigated the low-lying electronic states of CeH by *ab initio* multiconfiguration/multireference approach. The SA-CASSCF calculation, followed by NEVPT2 calculation with a strongly-contracted scheme,[16–18,21] was carried out for the low-lying doublet and quartet states of CeH with all-electron relativistic basis sets, Sapporo-DKH3-*x*ZP-2012 for Ce,[8] and Sapporo-*x*ZP-2012 for H[9] (*x* = D, T, Q), with the third-order Douglas-Kroll one-electron integrals[22] for the scalar relativistic effect. The basis set of Sapporo-DKH3-QZP-2012 for Ce involves (13s11p9d7f4g3h1i). In the following, the combination of the Sapporo-DKH3-*x*ZP-2012 for Ce and Sapporo-*x*ZP-2012 for H is simply referred to as *x*ZP. The SA-CASSCF method was employed for doublet states and quartet states with the active space of 5 electrons in 14 orbitals (Ce-4f, 5d, 6s, and H-1s). In the NEVPT2 calculations, 4s, 4p, 4d, 4f, 5s, 5p, 5d, and 6s orbitals of Ce and H-1s orbitals were included as correlated orbitals. In the Breit–Pauli Hamiltonian scheme,[23] the spin-orbit coupling matrix was generated based on the SA-CASSCF wavefunction, and then, the SA-CASSCF energies for the respective electronic states in the diagonal terms were substituted by the corresponding NEVPT2 energies followed by a diagonalization of the resultant spin-orbit coupling matrix to evaluate the energy levels of the spin-orbit-coupled states. The similar approach was applied successfully to *ab initio* calculations of the low-lying states of PtCN/PtNC, PdCN/PdNC,[24] Ce^+, and CeF.[15] The Ce-H bond length and stretching frequency were evaluated for the ground state by solving the one-dimensional ro-vibrational Schrödinger equation, using the VIBROT code in MOLCAS.[25] All the electronic structure calculations were carried out with the Molpro2012 program package.[26,27]

Results and discussion

For CeH, the previous theoretical studies suggested two possibilities for the electronic ground state, doublet[19] or quartet.[20] To determine the true ground state, one needs to consider the spin-orbit coupling effect. Through the SA-CASSCF and NEVPT2 calculations with a state-average scheme, we verified that the dominant electronic configurations in the lowest-lying doublet states and quartet states are $4f^1(5d_\sigma\text{-}H_{1s})^2 6s^2$ and $4f^1 5d^1(5d_\sigma\text{-}H_{1s})^2 6s^1$, respectively. The electronic term of Ce in CeH is ^2F for $4f^1(5d_\sigma\text{-}H_{1s})^2 6s^2$ and ^4H for $4f^1 5d^1(5d_\sigma\text{-}H_{1s})^2 6s^1$, and thus, we decided to carry out SA-CASSCF and following NEVPT2 calculations for seven doublet and eleven quartet states. Fig. 1 shows the Ce-H (a) bonding and (b) anti-bonding natural orbitals mainly consisting of Ce $5d_\sigma$ and H 1s, determined for quartet state at r(CeH) = 2 Å by the SA-CASSCF method with DZP basis sets. Their occupation numbers are also given in parentheses. The feature of these orbitals is the same as that for doublet state. The almost equivalent contributions of Ce $5d_\sigma$ and H 1s orbitals in these orbitals indicate a covalent nature for Ce-H bond.

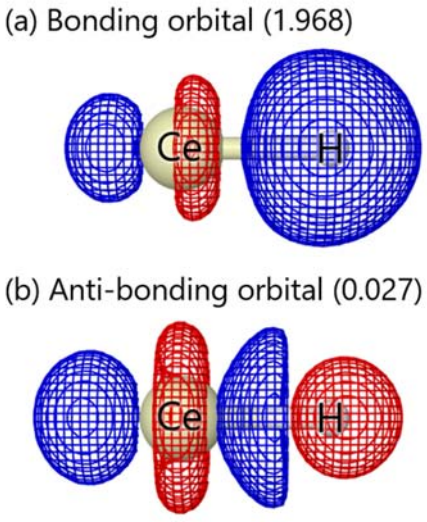


Fig. 1 Ce ($5d_\sigma$)-H (1s) natural orbitals with (a) bonding and (b) anti-bonding characters for quartet state by the SA-CASSCF method with DZP basis set. The natural orbital occupations are given in parentheses.

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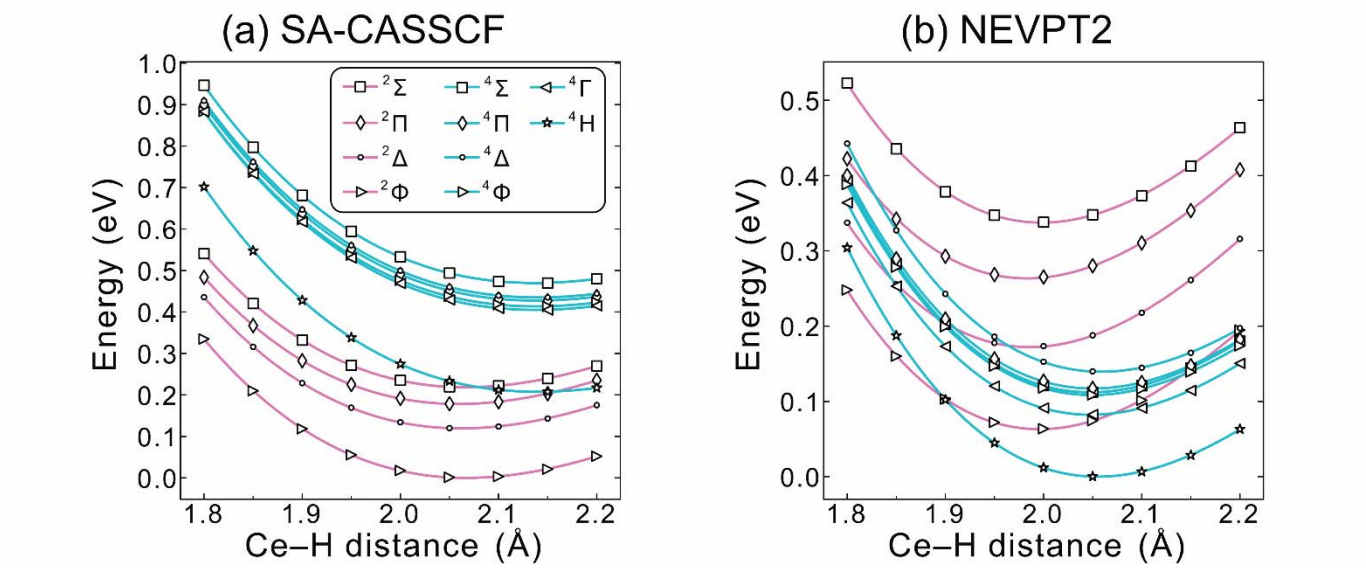


Fig. 2 (a) The SA-CASSCF and (b) NEVPT2 potential energy curves of the low-lying seven doublet and eleven quartet states of CeH diatomic molecule determined with QZP basis sets where the energy level of the minimum of the lowest state is set to be zero at the respective computational levels.

Fig. 2 shows the potential energy curves of the seven doublet ($^2\Sigma$, $^2\Pi$, $^2\Delta$, $^2\Phi$) and eleven quartet ($^4\Sigma$, $^4\Pi$, $^4\Delta$, $^4\Phi$, $^4\Gamma$, ^4H) states calculated by the SA-CASSCF and NEVPT2 methods with QZP basis sets for CeH diatomic molecule. It is noted that the Π, Δ, Φ, Γ, and H states are doubly-degenerate, respectively. The energy range of these low-lying doublet and quartet states is quite small, and the ground state character is different between the SA-CASSCF and NEVPT2 levels. At the SA-CASSCF level, the ground state is doublet with the lowest quartet state minimum lying 0.21 eV above; by including dynamic correlation effect through the NEVPT2 calculation, a group of the quartet states are stabilized relative to the doublet states, and the ground state changes to quartet with the doublet state minimum lying 0.06 eV above. The dynamic correlation effect works to shorten the equilibrium bond lengths for both doublet and quartet states. A group of potential energy curves of the same spin-multiplicity (doublet or quartet) show an almost parallel feature, and the potential minimum is calculated to be 1.996 Å (doublet) and 2.055 Å (quartet) at the NEVPT2 level.

In general, one would expect the dynamical correlation effect to be larger in the doublet state than in the quartet state, but this is not the case in CeH. This can be understood by considering the difference in electron configuration between the doublet ($4f^1(5d_\sigma\text{-}H_{1s})^2 6s^2$) and quartet ($4f^1 5d^1(5d_\sigma\text{-}H_{1s})^2 6s^1$) states. That is, the 6s orbital is spatially more extended than the other orbitals, and the dynamic correlation between the 6s electrons and the other valence electrons is not as large, indicating that the electron correlation effect is greater in the quartet state ($5d^1 6s^1$) than in the doublet state ($6s^2$). Actually, in our previous study on CeF,[15] we carried out state-averaged restricted active space multiconfigurational self-consistent field (SA-RASSCF) and NEVPT2 calculations for two different configurations of quartet of Ce^+, i.e., $[Xe]4f^1 5d^2$ (ground state) and $[Xe]4f^1 5d^1 6s^1$ (excited state), and verified that the relative energy of the lowest electronic states of the respective configurations were 0.187 eV (SA-RASSCF) and 0.292 eV (NEVPT2), indicating the smaller electron correlation of 6s electron than that of 5d electron.

The shorter bond distance in the doublet state than in the quartet state can be explained intuitively by the difference in electronic configuration in each state: the valence orbitals of Ce that can interact with H-1s are 6s and $5d_\sigma$ of σ-symmetry; Ce-$5d_\sigma$ and H-1s form a bonding orbital as shown in Fig. 1, which is occupied by two electrons in both the quartet and doublet states. Ce-6s is also slightly mixed with H-1s in-phase, and since Ce-6s occupies one electron in the quartet state and two electrons in the doublet state, it is suggested that the Ce-H bond is slightly stronger and the bond length is shorter in the doublet state than in the quartet state.

We also performed the same SA-CASSCF and NEVPT2 calculations using DZP and TZP basis sets to examine the basis set effects on the relative energy of the doublet and quartet states of Ce-H. The profiles of potential energy curves are independent of the basis sets, but the relative stability of doublet and quartet states changes depending on the basis sets. In NEVPT2 calculations, the relative energy of the lowest doublet minimum with respect to the lowest quartet minimum is -0.16 eV (DZP), -0.04 eV (TZP), and 0.06 eV (QZP), and therefore, the basis sets of QZP quality is required to reproduce the correct spin multiplicity of the ground state; the calculations with the DZP and TZP basis sets predict the ground state to be doublet. Hereafter, only the results of calculations with QZP basis sets are shown.

Next, we turn to the spin-orbit coupled states generated from the seven doublet ($^2\Sigma$, $^2\Pi$, $^2\Delta$, $^2\Phi$) and eleven quartet ($^4\Sigma$, $^4\Pi$, $^4\Delta$, $^4\Phi$, $^4\Gamma$, ^4H) states. The number of the generated spin-orbit coupled states are 58 which is equal to a summation of 2 × 7 (doublet) + 4 × 11 (quartet). The spin-orbit coupled states are

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distinguished by Ω, *i.e.*, a quantum number for the total electronic angular momentum around the molecular axis, assigned to the linear molecule. The target spin-orbit coupled states are Ω = 0.5 (6 states), Ω = 1.5 (6 states), Ω = 2.5 (6 states), Ω = 3.5 (5 states), Ω = 4.5 (3 states), Ω = 5.5 (2 states), and Ω = 6.5 (1 states). It is noted that all the spin-orbit coupled states with non-zero Ω are doubly-degenerate, respectively, which can be expected from Kramers theorem.[28]

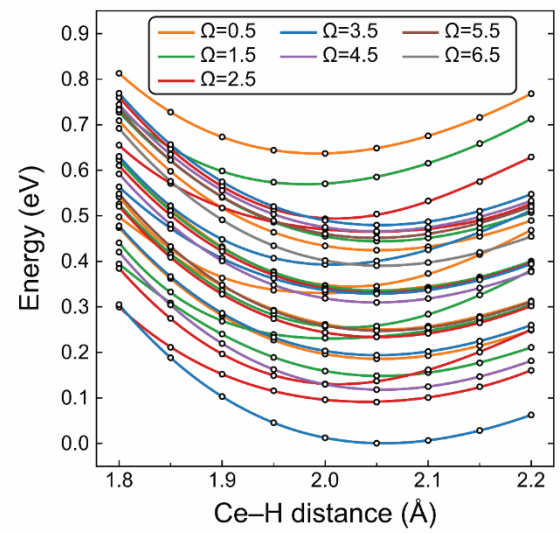


Fig. 3 The potential energy curves of the 58 spin-orbit coupled states of CeH calculated by NEVPT2+SOCI. The respective stets are distinguished by Ω.

Fig. 3 shows the potential energy curves for the 58 spin-orbit coupled states of CeH diatomic molecule generated from NEVPT2+SOCI single-point calculations in a range of *r*(Ce-H) = 1.8–2.2 Å with a step of 0.05 Å. As shown in Fig. 3, the 58 spin-orbit coupled states are lying within a very narrow energy region of 0.7 eV. The ground state is verified to be a pure quartet state (Ω = 3.5) through an entire range of the Ce-H bond length. The first excited state (Ω = 2.5) shows a mixing nature of doublet and quartet; in a short bond length, it is a doublet dominant while it changes to a quartet dominant in a long bond length.

Through the spin-orbit couplings, the doublet states can contribute to the spin-orbit coupled states of Ω = 0.5, 1.5, 2.5, and 3.5, while the quartet states can contribute to those of Ω = 0.5, 1.5, 2.5, 3.5, 4.5, 5.5, and 6.5. Fig. 4 shows the NEVPT2+SOCI potential energy curves of the spin-orbit coupled states of Ω = 0.5, 1.5, 2.5, and 3.5, separately, which can consist of both doublet and quartet states. The number of doublet states is two (Ω = 0.5), two (Ω = 1.5), two (Ω = 2.5), and one (Ω = 3.5). In the respective potential energy curves, the mixing of doublet and quartet states is represented by the color in a gradation manner between the doublet (violet) and quartet (blue) states. The potential energy profiles in Fig. 4 clearly show that the doublet and quartet potential energy curves mix in at the crossing point regions, resulting in an avoided-crossing feature.

To show the mixing rate of doublet and quartet states more clearly, we plot the rate of the doublet state as a function of the Ce-H interatomic distance for the respective potential energy

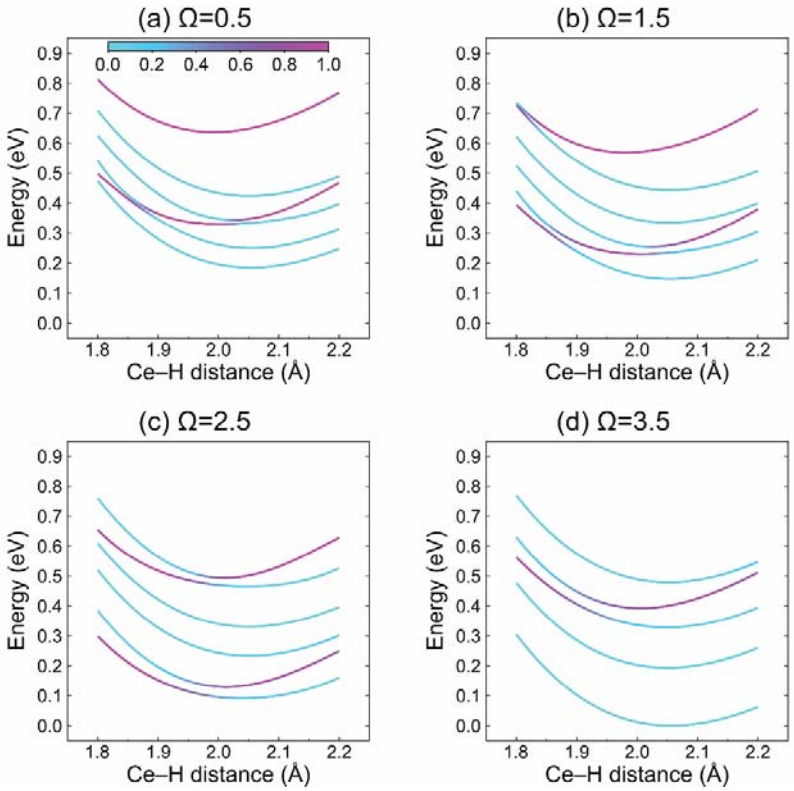


Fig. 4 The potential energy curves of the spin-orbit coupled states of (a) Ω = 0.5, (b) Ω = 1.5, (c) Ω = 2.5, and (d) Ω = 3.5, determined by NEVPT2+SOCI calculations. In the respective potential energy curves, the mixing of doublet and quartet states is represented by the color in a gradation manner between the doublet (violet) and quartet (blue) states.

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curves in Fig. 5. In a case of Ω = 0.5, the mixing of doublet and quartet states is not strong, and the sharp crossing appears at *r*(Ce-H) = 1.86 Å and 2.04 Å, respectively. In the other cases of Ω = 1.5, 2.5, and 3.5, however, the doublet and quartet states mix in effectively at the crossing region, and the rate of doublet state changes smoothly.

For the ground state of CeH with Ω = 3.5, we solved the ro-vibrational Schrödinger equation to evaluate the bond length in the zero-point vibrational state and fundamental frequency, using an option of VIBROT in the Molcas program. As for the potential energy curve with the Ce-H bond length longer than 2.2 Å, we could not get a converged SA-CASSCF result for the target seven doublet and eleven quartet states because the doublet states of $4f^15d^1(5d_\sigma\text{-}H_{1s})^26s^1$ configuration enter the averaged states, instead of the doublet states of $4f^1(5d_\sigma\text{-}H_{1s})^26s^2$ configuration. The fundamental frequency can be calculated as an energy difference of the vibrational ground and first-excited states. First, we verified that the ground state potential energy curve at the NEVPT2 level completely agrees with the corresponding curve determined at the NEVPT2+SOCI level, because the ground state is a pure quartet state. Then, we determined the potential energy curve by the NEVPT2 calculation based on the SA-CASSCF wavefunction averaged over only eleven quartet states of $4f^15d^1(5d_\sigma\text{-}H_{1s})^26s^1$ configuration. We obtained the potential energy curves for the ground state of pure quartet in a range of *r*(Ce-H) = 1.8–2.4 Å, which covers the energy range of 0–0.3 eV. The obtained potential energy curve at the NEVPT2 level was verified to reproduce the potential energy curve determined at the NEVPT2+SOCI level.

As the result of the VIBROT analysis, the equilibrium bond length and the bond length in the zero-point vibrational state were calculated to be 2.048 and 2.060 Å, respectively, and the harmonic frequency was calculated to be 1397 cm^{-1}. The energy levels of the vibrational ground state (zero-point vibrational state) and the first-excited state were calculated to be 0.086 eV and 0.253 eV, respectively, and thus, the fundamental frequency with the anharmonicity effect was evaluated as 1345 cm^{-1} (= 0.167 eV), which is in good agreement with the available experimental data, 1271 cm^{-1}, measured by a matrix-isolation technique.[20] A slight overestimation could be ascribed to the effects from the other low-lying spin-orbit coupled states and the matrix effects.

In the previous theoretical calculation,[20] the spin multiplicity of CeH was assumed to be quartet, and the Ce-H bond length and harmonic frequency were calculated to be 2.08 Å and 1311.8 cm^{-1}, respectively, by DFT with BP86 functional and basis sets of TZP quality. The calculated frequency shows better agreement with the experiment, although the present multireference calculations indicate that the quartet state is energetically higher than the doublet state with TZP basis set, and the correct ground state can only be reproduced by raising the quality of the basis set to QZP.

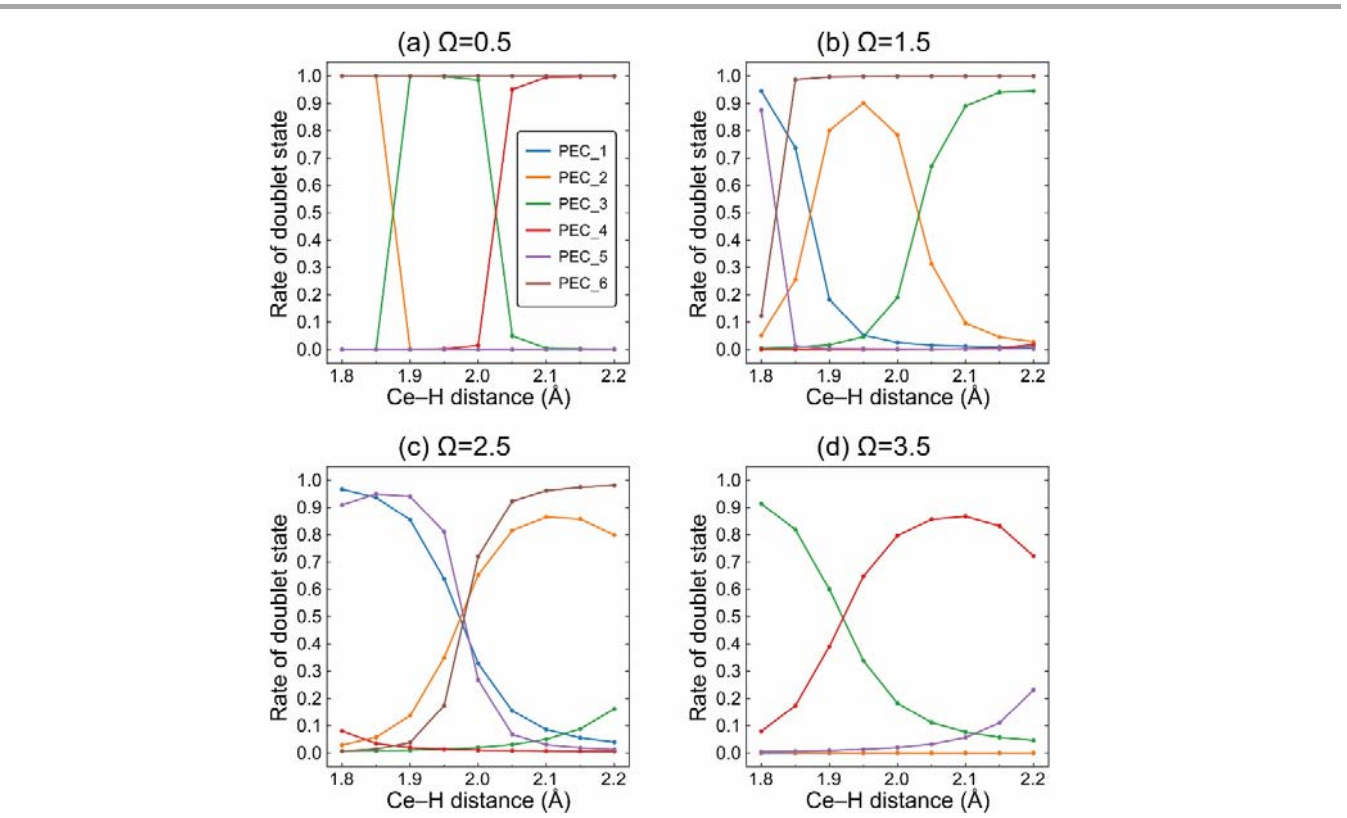


Fig. 5 The rate of doublet state in the spin-orbit coupled states as a function of the Ce-H bond length for (a) Ω = 0.5, (b) Ω = 1.5, (c) Ω = 2.5, and (d) Ω = 3.5, determined by NEVPT2+SOCI calculations. PEC_*n* denotes the potential energy curve of the *n*th electronic state in the respective Ω.

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Conclusions

In this paper, we employed the two-step spin-orbit approach using the SA-CASSCF and NEVPT2 plus SOCI calculations with the all-electron relativistic Sapporo basis sets, to investigate the spin-orbit coupled states consisting of the lowest-lying doublet states of $4f^1(5d_\sigma\text{-}H_{1s})^2 6s^2$ configuration and the quartet states of $4f^1 5d^1(5d_\sigma\text{-}H_{1s})^2 6s^1$ configuration. The previous theoretical studies could not determine the ground state of CeH to be quartet or doublet because of no consideration of the spin-orbit coupling effects. The present *ab initio* all-electron calculations clarified that the ground state of CeH is a pure quartet state with $\Omega = 3.5$. The examination of the basis set dependency of the spin multiplicity of the ground state indicated that the basis set of QZP quality is required to predict the correct ground state (quartet). The calculated Ce-H frequency in the quartet ground state is in good agreement with the experimental value measured in matrix isolation spectroscopy, confirming our conclusion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 E. Sanoyama, H. Kobayashi and S. Yabushita, *Journal of Molecular Structure: THEOCHEM*, 1998, **451**, 189–204.
2 W. C. Ermler, R. B. Ross and P. A. Christiansen, in *Advances in Quantum Chemistry*, ed. P.-O. Löwdin, Academic Press, 1988, vol. 19, pp. 139–182.
3 T. Tsuchiya, T. Taketsugu, H. Nakano and K. Hirao, *Journal of Molecular Structure: THEOCHEM*, 1999, **461-462**, 203–222.
4 J. Olsen, B. O. Roos, P. Jørgensen and H. J. A. Jensen, *J. Chem. Phys.*, 1988, **89**, 2185–2192.
5 M. Douglas and N. M. Kroll, *Ann. Phys.*, 1974, **82**, 89–155.
6 B. A. Hess, *Phys. Rev. A*, 1986, **33**, 3742–3748.
7 T. Nakajima and K. Hirao, *J. Chem. Phys.*, 2000, **113**, 7786–7789.
8 M. Sekiya, T. Noro, T. Koga and T. Shimazaki, *Theor. Chem. Acc.*, 2012, **131**, 1247.
9 T. Noro, M. Sekiya and T. Koga, *Theor. Chem. Acc.*, 2012, **131**, 1124.
10 Segmented GTF Basis Set, http://sapporo.center.ims.ac.jp/sapporo/, (accessed February 2020).
11 G. Schoendorff and A. K. Wilson, *J. Chem. Phys.*, 2014, **140**, 224314.
12 P. B. Armentrout, M. Demireva and K. A. Peterson, *J. Chem. Phys.*, 2017, **147**, 214307.
13 Q. Lu and K. A. Peterson, *J. Chem. Phys.*, 2016, **145**, 054111.
14 W. C. Martin, R. Zalubas and L. Hagan, *Atomic energy levels: The rare-earth elements (the spectra of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, ebrium, thulium, ytterbium, and lutetium)*, National Bureau of Standards, Washington, D.C., 1978
15 Y. Kondo, M. Kobayashi, T. Akama, T. Noro and T. Taketsugu, *J. Comput. Chem.*, 2018, **39**, 964–972.
16 C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger and J.-P. Malrieu, *J. Chem. Phys.*, 2001, **114**, 10252–10264.
17 C. Angeli, R. Cimiraglia and J.-P. Malrieu, *J. Chem. Phys.*, 2002, **117**, 9138–9153.
18 C. Angeli, M. Pastore and R. Cimiraglia, *Theor. Chem. Acc.*, 2007, **117**, 743–754.
19 M. Dolg and H. Stoll, *Theor. Chim. Acta*, 1989, **75**, 369–387.
20 S. P. Willson and L. Andrews, *J. Phys. Chem. A*, 2000, **104**, 1640–1647.
21 In the previous study on CeF (ref 15), we verified that only the NEVPT2 calculation with a strongly-contracted scheme reproduced the degeneracy of energies for the highly-degenerated electronic states of Ce^+ very well, so the strongly-contracted scheme is employed in this study.
22 A. Wolf, M. Reiher and B. A. Hess, *J. Chem. Phys.*, 2002, **117**, 9215–9226.
23 A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles and P. Palmieri, *Mol. Phys.*, 2000, **98**, 1823–1833.
24 Y. Ono, Y. Kondo, M. Kobayashi and T. Taketsugu, *Chem. Lett.*, 2016, **45**, 478–480.
25 F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov and R. Lindh, *J. Comput. Chem.*, 2010, **31**, 224–247.
26 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *WIREs Comput. Mol. Sci.*, 2012, **2**, 242–253.
27 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson and M. Wang, *MOLPRO, version 2012.1, a package of ab initio programs*, Cardiff, UK, 2012.
28 H. A. Kramers, *Proc. R. Neth. Acad. Arts Sci.*, 1930, **33**, 959–972.

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