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The *ab initio* ground-state potential energy function of beryllium monohydride, BeH

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The accurate ground-state potential energy function of beryllium monohydride, BeH, has been determined from large-scale *ab initio* calculations using the multi-reference averaged coupled-pair functional (MR-ACPF) method in conjunction with the correlation-consistent core-valence basis sets up to septuple-zeta quality. The effects of electron correlation beyond the MR-ACPF level of approximation were taken into account. The scalar relativistic and adiabatic (the diagonal correction) effects, as well as some of the nonadiabatic effects, were also discussed. The vibration-rotation energy levels of three isotopologues, BeH, BeD, and BeT, were predicted to sub-cm^{-1} accuracy. © *2011 American Institute of Physics*. [doi:10.1063/1.3671610]

I. INTRODUCTION

Beryllium monohydride, BeH, is a small heteronuclear radical, and the vibration-rotation energy levels of its ground electronic state $X\,^2\Sigma^+$ have been experimentally characterized nearly up to the dissociation limit (see Ref. 1, and references therein). Because it consists of only two nuclei and five electrons, the BeH radical is an attractive benchmark molecule for *ab initio* methods, and therefore, it has been the subject of numerous theoretical studies.[2–24] In the first calculation at the Hartree-Fock (HF) level of theory by Cade and Huo,[2] the ground-state potential energy function of BeH was determined. The binding energy D_e, the equilibrium internuclear distance r_e, and the vibrational fundamental wavenumber ν of BeH were calculated to be 17 600 cm^{-1}, 1.338 Å, and 2078 cm^{-1}, respectively, the values being amusingly close to the recent experimental data. In the following study by Chan and Davidson,[3] the role of electron correlation in determining the electronic structure of BeH was discussed and the potential energy functions for various excited states of BeH were calculated applying the configuration interaction approach. Mulliken[6] showed that the ground-state HF wave function of BeH exhibits discontinuous behavior at the internuclear distance of about 2.3 Å. This qualitative change in the bonding nature results in an artificial barrier in the ground-state potential energy function of BeH.[8,15,19] The artificial barrier disappears only when the electron correlation effects of BeH are nearly fully accounted for. The most extensive *ab initio* calculation on BeH to date was reported by Pitarch-Ruiz *et al.*[24] The all-electron full-configuration-interaction (FCI) method with the atomic natural orbital (ANO) basis sets of triple-zeta quality, augmented with diffuse Rydberg functions, was used to determine the potential energy functions for the ground and various excited states of BeH. For the ground state, various *spdf* basis sets were applied, but none of these was found to satisfactorily reproduce the spectroscopic constants of BeH.

Particularly, using the largest ANO basis set of quintuple-zeta quality, the spectroscopic constants D_e, r_e, and ν were determined to be 19 230 cm^{-1}, 1.322 Å, and 2166 cm^{-1}, respectively. Surprisingly enough, of the ANO basis sets considered by Pitarch-Ruiz *et al.*,[24] the largest one appeared to be the worst in predicting the ground-state potential energy function of BeH.

The aim of the present study is to provide the accurate *ab initio* potential energy function for the ground electronic state of beryllium monohydride and to discuss the effects which should be taken into account in order to predict the vibration-rotation energy levels of BeH with high accuracy.

II. METHOD OF CALCULATION

The molecular parameters of BeH were determined in this study using the multi-reference averaged coupled-pair functional (MR-ACPF) method[25,26] in conjunction with the augmented correlation-consistent core-valence basis sets up to septuple-zeta quality, aug-cc-pCVnZ (n = D − 7). The MR-ACPF method is an approximately size-extensive variant of the multi-reference configuration interaction approach including single and double excitations. The calculations consisted of the complete-active-space self-consistent-field (CASSCF) step followed by the internally contracted[27] MR-ACPF step. The usual full-valence active space, consisting of the 2s- and 2p-like orbitals of the beryllium atom and the 1s-like orbital of the hydrogen atom, appeared to be not adequate. Therefore, it was extended with the 3s- and 3p-like orbitals of the beryllium atom. The CASSCF wave function of BeH included, thus, all excitations of 3 valence electrons in 9 molecular orbitals. The reference function for the MR-ACPF calculation consisted of the CASSCF orbitals, resulting in 80 reference configuration state functions for the $X\,^2\Sigma^+$ state. The 1s-like orbital of the beryllium atom was kept doubly occupied in all reference configuration state functions; however, all of these orbitals were correlated through single and double excitations.

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The basis sets for beryllium consisted of the valence cc-pVnZ basis sets augmented with sets of diffuse (aug) and tight (C) functions. The valence cc-pVnZ basis sets up to quintuple-zeta quality were developed by Prascher *et al.*[28] The largest basis set for beryllium, cc-pV5Z, consists of a $(14s8p4d3f2g1h)/[6s5p4d3f2g1h]$ set. The cc-pV6Z basis set, consisting of a $(16s9p5d4f3g2h1i)/[7s6p5d4f3g2h1i]$ set, was developed for the study on the potential energy surface of BeH_2.[29] The cc-pV7Z basis set, consisting of a $(20s13p6d5f4g3h2i1k)/[8s7p6d5f4g3h2i1k]$ set, was developed for the study on the potential energy function of the beryllium dimer.[30] The basis sets for hydrogen consisted of the valence cc-pVnZ basis sets augmented with sets of diffuse (aug) functions.[31–33] The calculations were performed using the MOLPRO–2010 package of *ab initio* programs.[34] Because the MOLPRO package cannot handle k functions, these functions were omitted in the calculations with the aug-cc-pCV7Z basis set. Only the spherical harmonic components of the d through i polarization functions were used.

For accurately describing electron distribution at large distances, the basis sets augmented with diffuse functions, aug-cc-pVnZ, were used. The diffuse functions for beryllium, up to quintuple-zeta quality, were developed by Prascher *et al.*[28] For the aug-cc-pV6Z and aug-cc-pV7Z basis sets, the customary even-tempered exponents were calculated in this work by multiplying the exponent of the outermost primitive function of a given angular symmetry in the valence basis set by a factor of 0.4.

To account for the correlation effects of the $1s$ core electrons of the beryllium atom, the basis sets were further augmented with tight functions, aug-cc-pCVnZ. Groups of the primitive tight functions were added to the valence cc-pVnZ basis set. Prascher *et al.*[28] determined the largest core-valence basis set cc-pCV5Z for beryllium by augmenting the cc-pV5Z basis set with a $(4s4p3d2f1g)$ set. The cc-pV6Z and cc-pV7Z basis sets were augmented with the $(5s5p4d3f2g1h)$ and $(6s6p5d4f3g2h1i)$ sets, respectively.[30] Using the MR-ACPF method with all electrons correlated, the ground-state total energy of the beryllium atom was calculated to be -14.666541, -14.666909, and -14.667072 E_h for the aug-cc-pCV5Z, aug-cc-pCV6Z, and aug-cc-pCV7Z(i) basis set, respectively. The latter value is by 283 μE_h larger than the nonrelativistic energy of -14.667355 E_h predicted by Komasa *et al.*[35] in the variational calculations using a large basis set of explicitly-correlated Gaussian functions. The effect of the k functions omitted in the aug-cc-pCV7Z(i) basis set was addressed in the calculation for the beryllium atom using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T). The calculation was performed using the DALTON package of *ab initio* programs,[36] and this effect appeared to be small. The difference in the CCSD(T) ground-state total energy of Be, calculated using the aug-cc-pCV7Z basis set with and without the k functions, was found to be just 4.1 μE_h.

The vibration-rotation energy levels of three isotopologues, BeH, BeD, and BeT, were calculated using the Numerov-Cooley method.[37] The energy levels were calculated using the nuclear masses of beryllium and hydrogen.

TABLE I. Molecular parameters for the $X^2\Sigma^+$ state of BeH determined at the MR-ACPF/aug-cc-pCVnZ level of theory.

	$n = $ Q	$n = 5$	$n = 6$	$n = 7$
r_e[a](Å)	1.34198	1.34147	1.34115	1.34104
$E+15$[b](hartree)	-0.245941	-0.247118	-0.247617	-0.247833
D_e[c](cm^{-1})	17 621	17 683	17 711	17 723
ν[d](cm^{-1})	1984.17	1986.04	1987.21	1987.68
B_0[e](cm^{-1})	10.1768	10.1851	10.1898	10.1914

[a]The equilibrium internuclear distance.
[b]The total energy at a minimum.
[c]The binding energy.
[d]The vibrational fundamental wavenumber.
[e]The ground-state effective rotational constant.

III. RESULTS AND DISCUSSION

To determine the shape of the potential energy function of BeH, the total energies were calculated at the MR-ACPF/aug-cc-pCVnZ ($n = $ Q $-$ 7) level of theory, with all electrons correlated, at 48 internuclear distances ranging from 0.6 to 20 Å. The molecular parameters of $X^2\Sigma^+$ BeH thus derived are given in Table I. The parameters quoted include the equilibrium internuclear distance r_e, the total energy at minimum, the binding energy D_e, the vibrational fundamental wavenumber ν, and the ground-state vibrationally averaged (effective) rotational constant B_0. For a given vibrational state, the effective rotational constant B_v was determined by fitting the predicted rotation energies with a power series in $J(J + 1)$, where J is the rotational quantum number. The predicted values tend clearly to converge with enlargement of the basis set. The changes in the calculated equilibrium distance r_e and the binding energy D_e beyond the aug-cc-pCV7Z(i) basis set are estimated to be about 0.0001 Å and 10 cm^{-1}, respectively. The analogous changes in the vibrational fundamental wavenumber ν and the effective rotational constant B_0 are estimated to be about 0.5 and 0.002 cm^{-1}, respectively. The best potential energy function of $X^2\Sigma^+$ BeH, determined at the MR-ACPF/aug-cc-pCV7Z(i) level, is referred further to as "CV."

To address the question of the basis-set-superposition error (BSSE), the interaction energy of the beryllium and hydrogen atoms was calculated using the counterpoise method.[38] Because the MR-ACPF method is only approximately size-extensive, the calculations were performed at the CCSD(T)/aug-cc-pCVnZ ($n = 5 - 7$) level of theory, with all electrons correlated. At the internuclear distance of 1.34 Å, the counterpoise correction to the interaction energy was determined to be 4.1, 1.7, and 1.0 cm^{-1} for $n = 5$, 6, and 7, respectively. The size-extensivity error of the MR-ACPF method was determined by comparing the total energy of the BeH molecule, calculated for the internuclear distance of 100 Å, with the sum of the total energies of the isolated beryllium and hydrogen atoms. Using the aug-cc-pCVnZ basis sets with $n = 5$, 6, and 7, the size-extensivity error was determined to be 2.8, 2.9, and 1.5 cm^{-1}, respectively. In the vicinity of the equilibrium configuration of $X^2\Sigma^+$ BeH, the basis-set-superposition and size-extensivity errors, determined at the highest level of theory used in this work, are by the order of

TABLE II. Molecular parameters[a] for the $X^2\Sigma^+$ state of BeH determined using various potential energy functions.

	CV[b]	CV+F[c]	CV+F+R[c]	CV+F+R+D[c]	Exp.[d]
r_e(Å)	1.34104	1.34107	1.34099	1.34144	1.342394
$E+15$(hartree)	−0.247833	−0.247846	−0.250386	−0.249133	
D_e(cm^{-1})	17 723	17 730	17 722	17 702	17 590
ν(cm^{-1})	1987.68	1987.51	1987.48	1986.55	1986.416
B_0(cm^{-1})	10.1914	10.1910	10.1922	10.1853	10.16571

[a]See Table I.
[b]The potential energy function was calculated at the MR-ACPF/aug-cc-pCV7Z(i) level of theory.
[c]Including additionally the FCI (F), scalar relativistic (R), and diagonal Born-Oppenheimer (D) corrections (see the text).
[d]The experimental values from Ref. 1.

magnitude smaller than the estimated uncertainty in the binding energy D_e. Therefore, both errors are not significant and can be neglected.

To estimate the effects of electron correlation beyond the MR-ACPF level of approximation, full-configuration-interaction[39] calculations were performed, with all electrons correlated. At such a computationally demanding level of theory, only the aug-cc-pCVnZ basis sets of double- and triple-zeta quality could be applied. At each point of the potential energy function of BeH, the total energy was calculated using the FCI and MR-ACPF methods, both with the aug-cc-pCVnZ (n = D and T) basis sets and all electrons correlated. Differences between the FCI and MR-ACPF total energies of BeH were found to be small for all of the internuclear distances under consideration, not exceeding 30 and 40 μE_h for the n = D and T basis sets, respectively. The potential energy function of BeH was corrected for these effects by adding the differences between the FCI/ and MR-ACPF/aug-cc-pCVTZ total energies to the total energies of BeH calculated previously at the MR-ACPF/aug-cc-pCV7Z(i) level. This function is referred further to as "CV+F."

The potential energy function of BeH was further corrected for the scalar relativistic effects. These effects were investigated using the second-order Douglas-Kroll-Hess (DKH) one-electron Hamiltonian.[40,41] The relativistic contributions to the total energy were calculated using the MR-ACPF method with the uncontracted aug-cc-pCVQZ basis set, and with all electrons correlated. At each point of the potential energy function of BeH, the relativistic correction was determined as the difference in the total energy calculated using either the DKH or the nonrelativistic Hamiltonian. The inclusion of the scalar relativistic effects lowers the total energy of BeH by about 2.5 mE_h. The relativistic correction was found to be nearly constant over the large range of the internuclear distance, varying by less than 0.07 mE_h along the calculated potential energy function of BeH. The relativistic corrections were added to the CV+F potential energy function of BeH, and this function is referred further to as "CV+F+R."

For each of the calculated potential energy functions of BeH mentioned above, the molecular parameters were then determined. The results are given in Table II and are compared with the recent experimental data reported by Le Roy *et al.*[1] The FCI and scalar relativistic corrections appeared to have little impact on the predicted values of the molecular parameters. The best Born-Oppenheimer potential energy function of BeH (CV+F+R) has a minimum at 1.3410 ± 0.0001 Å and the well depth of 17 720 ± 10 cm^{-1}. Although the binding energy D_e is predicted to be within the error bars of the experimental value of 17 590 ± 200 cm^{-1}, there is a significant discrepancy between the predicted and experimental equilibrium internuclear distance r_e for the $X^2\Sigma^+$ state of BeH. The latter parameter is recommended by Le Roy *et al.*[1] to be 1.342394 ± 0.000001 Å. The difference between the predicted and experimental values of r_e is an order of magnitude larger than the estimated theoretical uncertainty. Such a large discrepancy is somewhat unexpected at the level of theory used in this work. Moreover, the best Born-Oppenheimer equilibrium internuclear distance of 1.34099 Å is determined here to be essentially identical to that of 1.34104 Å predicted by Martin[16] using the CCSD(T) method. The reason for the aforementioned discrepancy is unclear. A fraction of the difference between the predicted and experimental value of r_e may be attributed to the adiabatic effects (see below). Relative energies of the predicted Born-Oppenheimer potential energy function for the $X^2\Sigma^+$ state of BeH are given in Table III. Using this potential energy function, the dissociation energy D_0 of the BeH isotopologue is determined to be 16 699 cm^{-1}.

To account for the adiabatic effects, the diagonal Born-Oppenheimer correction (DBOC) (Refs. 42–44) was calculated for three isotopologues: BeH, BeD, and BeT. The DBOC was determined using the spin-unrestricted (UHF) and spin-restricted open-shell Hartree-Fock (ROHF) methods, as well as using the restricted-active-space configuration interaction (RAS CI) (Ref. 45) method, all in conjunction with the aug-cc-pCVTZ basis set. The calculations were performed using the PSI3 package of *ab initio* programs.[46] As for the MR-ACPF wave function, the active space (RAS II) for the RAS CI wave function of BeH consisted of 9 molecular orbitals: the 2s-, 2p-, 3s-, and 3p-like orbitals of the beryllium atom and the 1s-like orbital of the hydrogen atom. Only the three valence electrons of BeH were correlated through single and double excitations. Some additional calculations were also performed at the CCSD/aug-cc-pCVTZ level of theory, with the UHF wave function as a reference function, using the CFOUR package of *ab initio* programs.[47] In the vicinity of the equilibrium configuration of BeH, the DBOC was determined to be 269 cm^{-1} (1.226 mE_h) with both UHF and ROHF methods. Upon the inclusion of electron correlation, the DBOC was determined to be 275 and 282 cm^{-1} with the RAS CI and

TABLE III. Relative energies[a] of the Born-Oppenheimer potential energy function (CV+F+R) for the $X\,^2\Sigma^+$ state of BeH.

r (Å)	Energy	r (Å)	Energy
0.60	105 169.63	1.50	−16 572.59
0.65	77 543.34	1.55	−15 868.72
0.70	55 670.88	1.60	−15 063.34
0.75	38 357.64	1.65	−14 183.71
0.80	24 675.42	1.70	−13 252.86
0.85	13 896.77	1.80	−11 313.00
0.90	5447.96	1.90	−9369.74
0.95	−1125.87	2.00	−7518.32
1.00	−6186.94	2.10	−5832.29
1.05	−10 024.96	2.20	−4366.71
1.10	−12 872.63	2.30	−3155.94
1.15	−14 917.62	2.40	−2208.98
1.20	−16 311.92	2.50	−1507.72
1.25	−17 179.13	2.60	−1013.23
1.30	−17 620.16	2.80	−456.87
1.32	−17 696.29	3.00	−221.85
1.33	−17 715.26	3.50	−72.13
1.34	−17 722.22	4.00	−41.65
1.35	−17 717.69	4.50	−24.90
1.36	−17 702.19	5.00	−14.32
1.37	−17 676.19	6.00	−4.74
1.38	−17 640.16	8.00	−0.75
1.40	−17 539.76	10.00	−0.19
1.45	−17 142.53	20.00	0.00

[a]In cm^{-1}, relative to the total energy of BeH at the internuclear distance of 100 Å.

CCSD method, respectively. Changes in the DBOC values with the internuclear distance of BeH are illustrated in Figure 1. The DBOC values determined with the ROHF method exhibit discontinuous behavior at the internuclear distance of about 2.3 Å. The rapid change in the DBOC value, clearly seen in Figure 1, is related to similar discontinuous behavior of the ROHF wave function of BeH found by Mulliken.[6] In contrast, a variation of the DBOC values determined with the RAS CI method is smooth because the RAS CI wave function includes all excitations of the three valence electrons of BeH. The DBOC values were calculated at the same set of points as the Born-Oppenheimer potential energy functions discussed above and were subsequently added to the CV+F+R total energies. The resulting mass-dependent adiabatic potential energy functions are referred further to as "CV+F+R+D." The predicted DBOC values are given in the supplementary material.[48] For the BeH, BeD, and BeT isotopologues, the adiabatic equilibrium internuclear distances are predicted to be longer than the Born-Oppenheimer equilibrium internuclear distance r_e by 0.00045, 0.00025, and 0.00018 Å, respectively. The adiabatic corrections to the Born-Oppenheimer binding energy D_e are predicted to be −20, −9, and −5 cm^{-1}, respectively. As shown in Table III, the adiabatic corrections to the molecular parameters of BeH appeared to be essential and were found to be nearly by the order of magnitude larger than the FCI and scalar relativistic corrections. In particular, upon the inclusion of the adiabatic corrections, the experimental fundamental wavenumber ν and the ground-state effective rotational constant B_0 of the BeH isotopologue were reproduced to about 0.1 and 0.02 cm^{-1}, respectively.
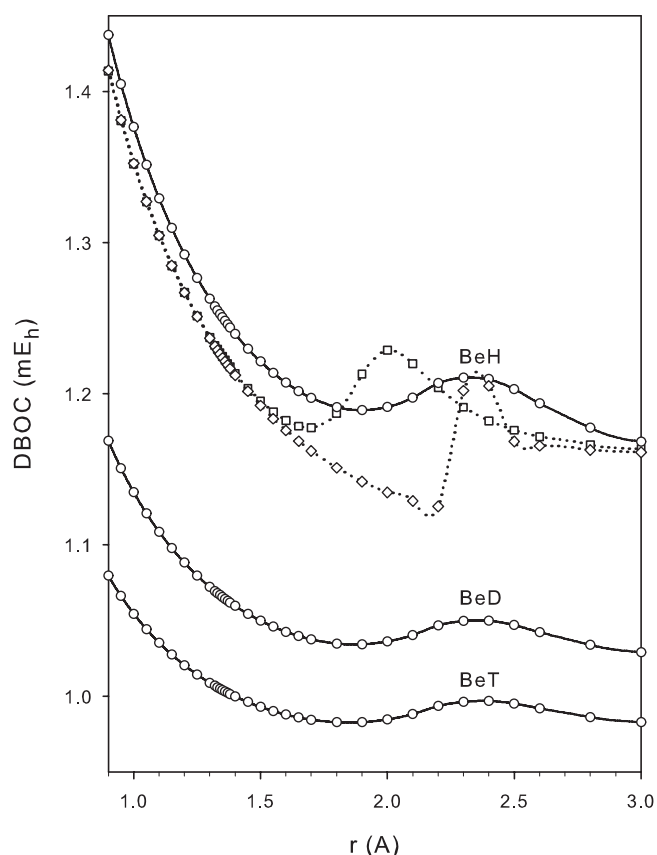

FIG. 1. The DBOC's for the $X\,^2\Sigma^+$ state of the BeH, BeD, and BeT isotopologues as functions of the internuclear distance r. The solid lines represent the DBOC values determined using a multi-reference wave function at the RAS CI/aug-cc-pCVTZ level of theory. The dotted lines represent the DBOC values for the BeH isotopologue determined using a single-reference wave function at the UHF/aug-cc-pCVTZ (squares) and ROHF/aug-cc-pCVTZ (diamonds) level of theory.

The adiabatic potential energy functions CV+F+R+D were used to determine all bound vibration-rotation energy levels for the $X\,^2\Sigma^+$ state of the BeH, BeD, and BeT isotopologues. The calculated vibrational term values T_v and the effective rotational constants B_v and quartic centrifugal distortion constants D_v are given in Tables IV–VI. The predicted values are compared with the experimental values reported by Le Roy *et al.*[1] The experimental data include 11, 13, and 4 vibrational energy levels for BeH, BeD, and BeT, respectively. The band constants for some higher excited vibrational states were also predicted by Le Roy *et al.*[1] Note, however, that uncertainties in the experimentally extrapolated band constants are much larger than those in the band constants of the observed vibrational energy levels.[49] Except for the highest observed vibrational energy level of BeH and BeD, the vibrational term values T_v of the BeH, BeD, and BeT isotopologues are predicted with the root-mean-square (rms) deviation $\bar\Delta$ of 0.44, 0.23, and 0.02 cm^{-1}, respectively. For all of the observed vibrational energy levels of the BeH, BeD, and BeT isotopologues, the effective rotational constants B_v are predicted with the rms deviation $\bar\Delta$ of 0.014, 0.005, and 0.004 cm^{-1}, respectively. The corresponding centrifugal distortion constants D_v are predicted with the rms deviation $\bar\Delta \times 10^3$ of 0.0406, 0.0126, and 0.0007 cm^{-1}, respectively.

TABLE IV. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^2\Sigma^+$ state of BeH.

v	T_v Exp.[a]	T_v Calc.[b]	T_v Δ[c]	B_v Exp.	B_v Calc.	B_v Δ	$D_v \times 10^3$ Exp.	$D_v \times 10^3$ Calc.	$D_v \times 10^3$ Δ
0	0.000	0.00		10.16571	10.1853	−0.0196	1.0272	1.035	−0.008
1	1986.416	1986.55	−0.13	9.85583	9.8748	−0.0190	1.0169	1.024	−0.007
2	3896.871	3897.10	−0.23	9.54172	9.5601	−0.0184	1.0104	1.018	−0.008
3	5729.260	5729.57	−0.31	9.22028	9.2377	−0.0174	1.0100	1.017	−0.007
4	7480.338	7480.68	−0.34	8.88674	8.9033	−0.0166	1.0170	1.024	−0.007
5	9145.132	9145.54	−0.41	8.53443	8.5499	−0.0155	1.0388	1.043	−0.004
6	10 716.163	10 716.76	−0.60	8.15377	8.1666	−0.0128	1.0940	1.083	0.011
7	12 182.207	12 182.86	−0.65	7.72826	7.7365	−0.0082	1.2072	1.163	0.044
8	13 525.788	13 526.22	−0.43	7.22531	7.2268	−0.0015	1.3992	1.317	0.082
9	14 718.082	14 717.49	0.59	6.57966	6.5782	0.0015	1.7158	1.627	0.089
10	15 709.384	15 706.72	2.66	5.66741	5.6628	0.0046	2.3896	2.356	0.034
11	(16 403.0)	16 400.35	2.65	(4.0486)	4.1320	−0.0834	(5.55)	4.755	0.795

[a]The experimental values from Ref. 1. The predicted values are given in parentheses.
[b]The values calculated using the adiabatic potential energy function CV+F+R+D (see the text). The experimental (extrapolated) and calculated zero-point energies are 1021.290 and 1022.33 cm^{-1}, respectively.
[c]A difference between the experimental and calculated values.

Concerning the effective rotational constants B_v, differences between the experimental and calculated values (Δ) tend to change systematically with excitation of the BeH stretching mode. The most prominent differences, from −0.0196 cm^{-1} for $v = 0$ to 0.0046 cm^{-1} for $v = 10$, are observed for the BeH isotopologue. For the BeD isotopologue, these differences extend over the smaller range, from −0.0068 cm^{-1} for $v = 0$ to 0.0031 cm^{-1} for $v = 12$, while for the BeT isotopologue, these differences are nearly constant, from −0.0039 cm^{-1} for $v = 0$ to −0.0037 cm^{-1} for $v = 3$.

The differences between the experimental and calculated values of the effective rotational constants B_v are clearly mass dependent and, therefore, they may be attributed to the neglected nonadiabatic effects. The importance of the nonadiabatic effects for BeH was already discussed by Martin.[16] As the first step to address this question, the rotational g-factor g_r was determined for various internuclear distances at the CASSCF/aug-cc-pCVTZ level of theory, with the active space consisting of 9 molecular orbitals of BeH. The calculations were performed using the DALTON package of *ab initio*

TABLE V. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^2\Sigma^+$ state of BeD.

v	T_v Exp.[a]	T_v Calc.[b]	T_v Δ[c]	B_v Exp.	B_v Calc.	B_v Δ	$D_v \times 10^3$ Exp.	$D_v \times 10^3$ Calc.	$D_v \times 10^3$ Δ
0	0.000	0.00		5.62526	5.6321	−0.0068	0.3129	0.314	−0.001
1	1488.842	1488.90	−0.06	5.49886	5.5055	−0.0066	0.3104	0.312	−0.002
2	2936.190	2936.27	−0.08	5.37147	5.3779	−0.0064	0.3084	0.310	−0.002
3	4341.375	4341.47	−0.10	5.24252	5.2488	−0.0063	0.3072	0.309	−0.002
4	5703.460	5703.54	−0.08	5.11125	5.1172	−0.0060	0.3071	0.308	−0.001
5	7021.155	7021.19	−0.04	4.97661	4.9823	−0.0057	0.3081	0.309	−0.001
6	8292.679	8292.64	0.04	4.83722	4.8427	−0.0055	0.3108	0.312	−0.001
7	9515.606	9515.50	0.11	4.69137	4.6965	−0.0051	0.3166	0.317	0.000
8	10 686.666	10 686.55	0.12	4.53676	4.5410	−0.0042	0.3283	0.326	0.002
9	11 801.447	11 801.31	0.14	4.36993	4.3727	−0.0028	0.3489	0.340	0.009
10	12 853.886	12 853.61	0.28	4.18520	4.1856	−0.0004	0.3812	0.363	0.018
11	13 835.380	13 834.73	0.65	3.97296	3.9709	0.0021	0.4277	0.401	0.027
12	14 733.329	14 731.94	1.39	3.71720	3.7141	0.0031	0.4944	0.464	0.030
13	(15 531.2)	15 526.42	4.78	(3.3907)	3.3904	0.0003	(0.574)	0.580	−0.006
14	(16 195.5)	16 188.82	6.68	(2.9501)	2.9501	0.0000	(0.823)	0.815	0.008
15	(16 673.6)	16 670.88	2.72	(2.2309)	2.2818	−0.0509	(1.68)	1.427	0.253
16		16 899.63			1.1771			2.959	

[a]The experimental values from Ref. 1. The predicted values are given in parentheses.
[b]The values calculated using the adiabatic potential energy function CV+F+R+D (see the text). The experimental (extrapolated) and calculated zero-point energies are 759.856 and 760.41 cm^{-1}, respectively.
[c]A difference between the experimental and calculated values.

TABLE VI. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X^2\Sigma^+$ state of BeT.

v	T_v Exp.[a]	T_v Calc.[b]	T_v Δ[c]	B_v Exp.	B_v Calc.	B_v Δ	$D_v \times 10^3$ Exp.	$D_v \times 10^3$ Calc.	$D_v \times 10^3$ Δ
0	0.000	0.00		4.10599	4.1099	−0.0039	0.1663	0.167	−0.001
1	1276.024	1276.05	−0.03	4.02745	4.0313	−0.0039	0.1652	0.166	−0.001
2	2521.903	2521.93	−0.03	3.94844	3.9522	−0.0038	0.1642	0.165	−0.001
3	3737.273	3737.29	−0.02	3.86873	3.8724	−0.0037	0.1635	0.164	−0.001
4	(4921.6)	4921.63	−0.03	(3.7880)	3.7915	−0.0035	(0.163)	0.164	−0.001
5	(6074.3)	6074.27	0.03	(3.7059)	3.7093	−0.0034	(0.163)	0.164	−0.001
6	(7194.4)	7194.32	0.08	(3.6219)	3.6251	−0.0032	(0.164)	0.164	0.000
7	(8280.9)	8280.67	0.23	(3.5353)	3.5384	−0.0031	(0.165)	0.165	0.000
8	(9332.1)	9331.83	0.27	(3.4454)	3.4483	−0.0029	(0.167)	0.167	0.000
9	(10 346.3)	10 345.90	0.40	(3.3512)	3.3537	−0.0025	(0.171)	0.171	0.000
10	(11 320.8)	11 320.40	0.40	(3.2513)	3.2532	−0.0019	(0.179)	0.176	0.003
11	(12 252.5)	12 252.03	0.47	(3.1438)	3.1445	−0.0007	(0.190)	0.184	0.006
12	(13 137.2)	13 136.47	0.73	(3.0256)	3.0247	0.0009	(0.206)	0.195	0.011
13		13 967.37			2.8895			0.218	
14		14 737.41			2.7318			0.245	
15		15 434.89			2.5411			0.289	
16		16 043.31			2.2981			0.371	
17		16 537.84			1.9672			0.531	
18		16 879.75			1.4689			0.947	
19		17 024.38			0.7513			1.447	

[a]The experimental values from Ref. 1. The predicted values are given in parentheses.
[b]The values calculated using the adiabatic potential energy function CV+F+R+D (see the text). The experimental (extrapolated) and calculated zero-point energies are 649.249 and 649.65 cm^{-1}, respectively.
[c]A difference between the experimental and calculated values.

programs.[36,50] The rotational g-factor (the electronic contribution g_r^{el}) was included by means of a second-order correction to the rotational term of the effective vibration-rotation Hamiltonian of a diatomic molecule.[51–53] Using the adiabatic potential energy functions CV+F+R+D, the ground-state effective rotational constant B_0 of the BeH, BeD, and BeT isotopologue was determined in this way to be 10.1650, 5.6260, and 4.1067 cm^{-1}, respectively. The differences between the experimental and calculated B_0 values were, thus, found to decrease to only −0.0007 cm^{-1} for all of the three isotopologues. Therefore, the nonadiabatic effects related to the rotational g-factor account nearly completely for the experimental vs calculated differences in the B_0 values observed for the adiabatic vibration-rotation energy levels. The vibrationally averaged rotational g-factor (the electronic contribution) $\langle g_r^{el} \rangle$ for the ground state of the BeH, BeD, and BeT isotopologue was determined to be −3.59, −1.95, and −1.43, respectively. A detailed discussion about the nonadiabatic effects is postponed to the future paper concerning the electronically excited states of BeH.

Using the adiabatic potential energy functions CV+F+R+D, the dissociation energy D_0 of the BeH, BeD, and BeT isotopologue was determined to be 16 680, 16 953, and 17 067 cm^{-1}, respectively. The former value is close to the dissociation energy of the BeH isotopologue of 16 652 cm^{-1} predicted by Bubin and Adamowicz[22] in the non-Born-Oppenheimer variational calculations using a large basis set of explicitly correlated Gaussian functions. The vibrationally averaged internuclear distance $\langle r \rangle$ for the ground state of the BeH, BeD, and BeT isotopologue

was determined to be 1.36182, 1.35630, and 1.35400 Å, respectively. The former value differs by only 0.00023 Å from the theoretical estimate of 1.36159 Å by Bubin and Adamowicz.[22]

In conclusion, the accurate potential energy function of beryllium monohydride in its ground electronic state $X^2\Sigma^+$ was determined in the state-of-the-art *ab initio* calculations, and the vibration-rotation energy levels of the BeH, BeD, and BeT isotopologues were predicted to sub-cm^{-1} ("spectroscopic") accuracy.

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[48]See supplementary material at http://dx.doi.org/10.1063/1.3671610 for the DBOC values predicted for the BeH, BeD, and BeT isotopologues at the RAS CI/aug-cc-pCVTZ level of theory.

[49]For example, the values of T_v (calculated relative to the extrapolated $v = -1/2$ energy level), B_v, and $D_v \times 10^3$ for the $v = 11$ state of the BeH isotopologue are given in Table 10 of Ref. 1 to be 17424.3, 4.0486, and 5.55 cm^{-1}, respectively, while in the supplementary data for that article, the corresponding values are quoted to be 17434.06, 4.26816, and 4.295 cm^{-1}, respectively.

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