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Ab Initio Prediction of the Potential Energy Surface and Vibrational−Rotational Energy Levels of X^2A' BeOH

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The equilibrium structure and potential energy surface of beryllium monohydroxide in its ground doublet state, X^2A' BeOH, have been determined from large-scale ab initio calculations using the spin-restricted coupled-cluster method, RCCSD(T), with basis sets of double- through quintuple-ζ quality. The BeOH radical was found to be quasilinear, with an equilibrium BeOH angle of 140.9° and a barrier to linearity of 136 cm^{-1}. The vibrational−rotational energy levels of various isotopomers were predicted using the variational method. The calculated spectroscopic constants should be useful in the future detection of beryllium monohydroxide by high-resolution vibrational−rotational spectroscopy.

1. Introduction

In the series of alkaline-earth monohydroxides, *M*OH (*M* = Be, Mg, Ca, ...), very little indeed is known about beryllium monohydroxide. The BeOH radical has been detected using electron-spin resonance (ESR)[1] and low-resolution infrared spectroscopy[2] in inert-gas matrices. The ESR spectrum was found[1] to be consistent with that characteristic of a linear molecule. A weak absorption band was observed[2] at 1245.5 cm^{-1} and tentatively assigned to the BeO stretching mode; no bands due to other vibrational modes were detected.

Theoretical studies on beryllium monohydroxide have been more numerous.[3−10] In contrast to other members of the series, the BeOH radical was predicted in early theoretical studies[3,4] to be bent at equilibrium. The valence BeOH angle was calculated to be 152 and 147° at the MP4/6-31+G**[3] and CISD/TZ2P[4] levels of theory, respectively. The barrier to linearity was predicted to be 46 and 60 cm^{-1}, respectively, thus indicating significant covalent character in the *M*−OH bonding. A bent equilibrium structure of the BeOH radical was also found in subsequent ab initio studies at the QCISD/6-311++G**,[5] CASSCF/TZ2P,[6] MRD-CI/TZ2P,[8] and MP2/6-311++G**[10] levels of theory as well as by density functional theory (DFT).[2,9] Surprisingly, a nearly linear equilibrium structure was predicted by Fernández[7] using the coupled-cluster method, CCSD(T),[11] based on an unrestricted Hartree−Fock (UHF) reference function. With an atomic natural orbital (ANO)[12] basis set of triple-ζ quality, their study[7] yielded an equilibrium BeOH angle of 179.5°. The harmonic frequencies for the BeOH radical have been calculated using various ab initio[5,6,10] and DFT[2,9] methods. In particular, the harmonic wavenumber for the BeOH bending mode (for the bent molecule) was predicted to be 389 cm^{-1} (QCISD/6-311++G**),[5] 422 cm^{-1} (CASSCF/TZ2P),[6] 347 cm^{-1} (MP2/6-311++G**),[10] 307 cm^{-1} (B3LYP/6-311G*),[2] and 368 cm^{-1} (B3PW91/6-311+G(2d,2p)).[9] To our knowledge, neither the experimental nor theoretical anharmonic force field of beryllium monohydroxide has been reported in the literature.

In this study, we present an accurate characterization of the potential energy surface and vibrational−rotational energy levels of beryllium monohydroxide. The molecular parameters are determined here by the ab initio approach using highly correlated wave functions calculated with large correlation-consistent spdfgh basis sets and taking into account core-electron correlation effects. This approach has been successfully applied previously to the predictions of the potential energy surfaces and vibrational−rotational energy levels of magnesium[13] and calcium[14] monohydroxides. For both MgOH and CaOH radicals, the calculated spectroscopic constants were found to be in remarkably good agreement with experimental data.

2. Method of Calculation

The molecular parameters of beryllium monohydroxide were calculated using the spin-restricted coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T).[15−17] The coupled-cluster wave function was based on spin-restricted Hartree−Fock (RHF) molecular orbitals as a reference function. The one-particle basis sets that were employed were the correlation-consistent polarized valence basis sets of double- through quintuple-ζ quality, cc-pVDZ through cc-pV5Z.[18,19] The largest basis set thus consisted of a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen and a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for beryllium and oxygen. Only the spherical harmonic components of the d through h polarization functions were used. In the correlation treatment, the 1s-like core orbitals of the beryllium and oxygen atoms were excluded from the active space unless otherwise noted.

The core-related correlation effects were investigated using the correlation-consistent core−valence basis sets, cc-pCV*n*Z.[19,20] Basis sets of triple- and quadruple-ζ quality were employed. The cc-pCV*n*Z basis sets were obtained by augmenting the standard cc-pV*n*Z basis sets with shells of tight functions. The largest basis set applied, cc-pCVQZ, was obtained by augmenting the cc-pVQZ basis set with a (3s3p2d1f) set for beryllium and oxygen.

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TABLE 1: Equilibrium Molecular Parameters of X^2A' BeOH Determined Using the RCCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(BeO) (Å)	1.4316	1.4099	1.4020	1.4022
r(OH) (Å)	0.9591	0.9522	0.9491	0.9490
∠(BeOH) (deg)	131.65	134.49	139.11	139.52
energy + 90 (hartrees)	−0.327398	−0.420733	−0.449253	−0.458332

TABLE 2: Molecular Parameters of the Linear Configuration of X^2A' BeOH Determined Using the RCCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(BeO) (Å)	1.4012	1.3821	1.3792	1.3798
r(OH) (Å)	0.9503	0.9448	0.9433	0.9433
ΔE^a (cm^{-1})	222	268	167	164

[a] ΔE is the energy difference between the linear and equilibrium configurations.

TABLE 3: Equilibrium Molecular Parameters of X^2A' BeOH Determined Using the RCCSD(T) Method with the cc-pCVTZ and cc-pCVQZ Basis Sets

	V	A	$A - V^a$
cc-pCVTZ			
r(BeO) (Å)	1.4076	1.4028	−0.0048
r(OH) (Å)	0.9518	0.9508	−0.0010
∠(BeOH) (deg)	134.37	135.33	0.96
energy (hartrees)	−90.425173	−90.523874	−0.098701
ΔE^b (cm^{-1})	275	247	−28
cc-pCVQZ			
r(BeO) (Å)	1.4015	1.3946	−0.0069
r(OH) (Å)	0.9492	0.9480	−0.0012
∠(BeOH) (deg)	139.09	140.51	1.42
energy (hartrees)	−90.450934	−90.558864	−0.107930
ΔE^b (cm^{-1})	168	140	−28

[a] The difference between the value determined correlating all of the electrons (A) and the value determined correlating only the valence electrons (V). [b] ΔE is the energy difference between the linear and equilibrium configurations.

The calculations were performed using the MOLPRO-2000 package of ab initio programs.[21]

The vibrational−rotational−spin energy levels were calculated variationally using the 6D Hamiltonian of a triatomic molecule developed by Carter and Handy.[22−25] The Hamiltonian consists of an exact representation of the kinetic energy operator and a representation of the potential energy operator in terms of valence curvilinear coordinates. Vibrational basis-set functions were formed as products of the contracted 2D stretching functions and 1D bending functions. For each value of the total angular momentum quantum number $J = N \pm S$, where N and S are the rotational and spin quantum numbers, respectively, the secular matrix was constructed using the vibrational expansion functions and the rotational symmetric-top functions. The matrix elements were evaluated by numerical quadrature. The secular matrix was then diagonalized to obtain the vibrational−rotational−spin energy levels. The number of contracted 2D stretching functions was 40, and the number of contracted bending functions was 20, leading to a total of 800 vibrational basis functions.

3. Results and Discussion

The equilibrium structural parameters and total energy computed for the ground electronic state of the BeOH radical are listed in Table 1. For all of the one-particle basis sets employed, the molecule is predicted to be bent at equilibrium, the electronic state thus being X^2A'. This is consistent with the results of previous theoretical studies on beryllium monohydroxide,[3−6,8−10] except for that by Fernández.[7] The reason for the apparent discrepancy with the nearly linear equilibrium structure found in their UCCSD(T)/ANO calculation[7] is not known. Moreover, the predicted equilibrium BeOH angle of 179.5° seems not to be a physically feasible result. One must instead consider that the UCCSD(T)/ANO calculation[7] describes the BeOH bending potential energy function as being perhaps very flat but with no barrier to linearity. Turning to the results of Table 1, changes in the calculated bond lengths beyond the quintuple-ζ basis set can be expected to be negligibly small, whereas that in the valence BeOH angle is estimated to be about ±0.2°. Changes in the total energy and structural parameters with the one-particle basis set thus indicate that the convergence is nearly complete with the cc-pV5Z basis set. Table 2 lists the molecular parameters calculated for the linear configuration of the BeOH radical. The height of the barrier to linearity is predicted in this work to be a factor of ∼3 higher than that found in previous theoretical studies.[3,4,8] The change in the calculated barrier height beyond the quintuple-ζ basis set is estimated to be only about ±2 cm^{-1}.

The core-related effects were computed as differences between the molecular parameters determined in calculations correlating only the valence electrons and those when all of the electrons were correlated; both calculations were performed with the same one-particle core-valence basis set. The results obtained with the cc-pCVTZ and cc-pCVQZ basis sets are given in Table 3. Inclusion of the core-related effects substantially changes the equilibrium BeO bond length and the valence BeOH angle, whereas the OH bond length is only slightly affected. The height of the barrier to linearity is predicted to decrease by 28 cm^{-1}.

The best estimates of the molecular parameters of beryllium monohydroxide can be determined by adding the changes in the parameters due to the core-related correlation effects (cc-pCVQZ of Table 3) to the values determined with the largest valence basis set (cc-pV5Z of Tables 1 and 2). The equilibrium structural parameters of the BeOH radical are estimated in this way to be r_e(BeO) = 1.395 Å, r_e(OH) = 0.948 Å, and $\angle_e$(BeOH) = 140.9°, whereas the barrier to linearity is calculated to be 136 cm^{-1}. It is worth noting that these values are essentially identical to those determined with the cc-pCVQZ basis set when correlating all of the electrons. Considering the convergence of the calculated values with the one-particle basis-set size and the effects of approximations inherent in the RCCSD(T) approach, the equilibrium bond lengths are believed to be accurate to ±0.001 Å. Uncertainties in the equilibrium BeOH angle and barrier height are estimated to be about ±0.3° and ±10 cm^{-1}, respectively.

To determine the shape of the potential energy surface of beryllium monohydroxide, the total energy was calculated with the cc-pV5Z basis set at 159 points in the vicinity of the equilibrium configuration. The computed energies ranged to approximately 12 000 cm^{-1} above the minimum. The potential energy surface was then approximated by a 3D expansion along the internal valence coordinates. The internal coordinates for the BeO and OH stretching modes were chosen as Simons−Parr−Finlan coordinates,[26] $q = (r - r_e)/r$, where r and r_e are the instantaneous and equilibrium bond lengths, respectively. For the BeOH bending mode, a curvilinear displacement coordinate was used.[27] It was defined as the supplement of the valence BeOH angle measured from a linear reference configuration. The coordinates for the BeO and OH stretching modes are referred to as q_1 and q_2, respectively, whereas that for the

TABLE 4: Anharmonic Force Field[a] of X^2A' BeOH

i	j	k	V[b]	$V + C$[c]
0	0	2	−0.002854	−0.002549
2	0	0	1.333420	1.342534
0	2	0	0.964337	0.965423
0	0	4	0.004439	0.004337
1	1	0	−0.020730	−0.019936
1	0	2	−0.098966	−0.099434
0	1	2	−0.022567	−0.022472
3	0	0	−0.797486	−0.799935
0	3	0	−0.152982	−0.152384
0	0	6	−0.000395	−0.000376
1	2	0	−0.021652	−0.020203
1	0	4	0.029519	0.029643
0	1	4	0.000438	0.000365
2	1	0	−0.073360	−0.072769
2	0	2	0.025053	0.025007
0	2	2	−0.029508	−0.029475
1	1	2	−0.000091	0.000071
4	0	0	−0.390731	−0.399108
0	4	0	−0.316107	−0.315576
0	0	8	−0.000031	−0.000034
1	3	0	−0.089644	−0.090706
1	0	6	−0.003550	−0.003525
0	1	6	−0.000517	−0.000510
3	1	0	−0.032735	−0.034288
3	0	2	0.002106	0.002226
0	3	2	−0.012444	−0.012605
2	2	0	−0.143368	−0.145788
2	0	4	0.000617	0.000647
0	2	4	0.006263	0.006231
1	1	4	0.021478	0.021320
1	2	2	−0.024478	−0.025517
2	1	2	0.005401	0.004737
0	5	0	−0.339115	−0.339042
0	0	10	0.000022	0.000022
2	0	6	−0.004767	−0.004833
0	2	6	−0.002417	−0.002424
1	1	6	−0.004034	−0.003997
1	2	4	0.021065	0.021262
2	1	4	0.010008	0.010204
2	2	2	0.063036	0.064219

[a] Expansion coefficients c_{ijk} of eq 1 in hartrees. The coordinates q_1 and q_2 are dimensionless, and q_3 is in radians. [b] Determined at the RCCSD(T)/cc-pV5Z level of theory. [c] Including corrections for the core−electron correlation effects determined at the RCCSD(T)/cc-pCVQZ level.

BeOH bending mode, as q_3. Thus, the potential energy surface of beryllium monohydroxide can be written as the polynomial expansion

$$V(q_1, q_2, q_3) = V_{\text{lin}} + \sum_{ijk} c_{ijk}\, q_1^i q_2^j q_3^k \tag{1}$$

where V_{lin} is the total energy at the linear configuration of the BeOH radical. The expansion coefficients c_{ijk} were determined from a least-squares fit of eq 1 to the computed total energies, and 40 coefficients appeared to be statistically significant. Optimized values of the expansion coefficients are listed in Table 4 under column heading V. The BeO and OH bond lengths for the reference configuration are 1.3798 and 0.9433 Å, respectively. The root-mean-square deviation of the fit was 4.1 μhartrees (0.9 cm^{-1}). Because the reference configuration was assumed to be linear, the exponent k (for the BeOH bending mode) takes only even values. Because the equilibrium configuration of the BeOH radical was in fact calculated to be bent, the quadratic force constant for the BeOH bending mode (the coefficient c_{002}) is negative.

To investigate the effects of core−electron correlation on the shape of the calculated potential energy surface, additional calculations were performed with the cc-pCVQZ basis set. The total energy of beryllium monohydroxide was computed at the same points as calculated previously, correlating either only valence electrons or all of the electrons. At each point, the difference between these total energies was calculated and added to the valence-only total energy computed with the cc-pV5Z basis set. The calculated potential energy surface, corrected in this way for the core-related effects, was also approximated by the polynomial expansion of eq 1. Optimized values of the expansion coefficients c_{ijk} are listed in Table 4 under the column heading $V + C$. The BeO and OH bond lengths for the reference configuration are 1.3744 and 0.9426 Å, respectively.

Both of the determined anharmonic force fields were used to calculate the vibrational−rotational spin energy levels of the main beryllium monohydroxide isotopomer, BeOH, and the three other isotopic species, namely, BeOD, Be^{18}OH, and Be^{18}OD. Calculated values of the fundamental wavenumbers and effective ground-state rotational constant B_0 are given Table 5. The spin-doubling splittings are omitted, and the averaged vibrational−rotational term values are quoted. In the traditional way, the energy levels were labeled with the quantum numbers v_1 and v_3 for the BeO and OH stretching modes, respectively. Because the barrier to linearity of the BeOH radical was found to be quite low, quantum numbers v_2 and l_2 for the doubly degenerate bending mode of a linear molecule were used to label the BeOH bending energy levels. Therefore, the BeOH bending fundmental ν_2 corresponds to the $N = 1$, $(v_1, v_2^{l_2}, v_3) = (0, 1^1, 0)$ energy level. The B_0 values were obtained by fitting an odd-order power series in $(N + 1)$ to the calculated rotational transition frequencies. The predicted wavenumber of the BeO stretching fundamental for the main BeOH isotopomer is close to 1245.5 cm^{-1}, which was observed by Thompson and Andrews[2] in solid argon. Out of two predicted values, the BeO stretching fundamental determined with the V anharmonic force field is closer to the experimental solid-state value. However, as shown in our previous studies on the MgOH[13] and CaOH[14] radicals, the spectroscopic constants determined with the $V + C$ anharmonic force field are expected to be the best estimates of experimental gas-phase data. The differences between the observed and calculated wavenumbers of 10−20 cm^{-1} are likely due to matrix effects. The ^{18}O isotopic shift of the BeO stretching fundamental was predicted with the V and $V + C$

TABLE 5: Fundamental Vibrational Wavenumbers ν (cm^{-1}) and Effective Ground-State Rotational Constant B_0 (MHz) for Various Isotopomers of X^2A' BeOH

	V[a]				$V + C$[a]			
	BeOH	BeOD	Be^{18}OH	Be^{18}OD	BeOH	BeOD	Be^{18}OH	Be^{18}OD
ν_1 (BeO stretch)	1256.3	1240.2	1234.5	1220.2	1268.1	1252.2	1246.1	1232.0
ν_2 (BeOH bend)	93.0	52.9	91.8	51.5	99.9	58.1	98.6	56.6
ν_3 (OH stretch)	3862.7	2852.4	3850.1	2833.5	3873.4	2861.3	3860.8	2842.2
ZPE[b]	2774.1	2200.1	2754.9	2178.7	2778.6	2203.8	2759.3	2182.3
B_0	38692	34475	37581	33756	38970	34666	37856	33948

[a] Determined using the corresponding anharmonic force field of Table 4. [b] The zero-point energy (in reference to a minimum of the potential energy surface).

TABLE 6: $N = l_2$ Vibrational−Rotational Term Values (cm^{-1}) and Changes in the Effective Rotational Constant B_v (MHz) for the Low-Lying Energy Levels of X^2A' BeOH and BeOD[a]

	BeOH		BeOD	
$(v_1, v_2^{l_2}, v_3)$	energy/*hc*	ΔB_v	energy/*hc*	ΔB_v
$(0, 0^0, 0)$	0.	0.	0.	0.
$(0, 1^1, 0)$	99.9	−32.0	58.1	116.3
$(0, 2^2, 0)$	267.0	−102.8	162.1	191.0
$(0, 2^0, 0)$	348.4	146.1	241.2	124.8
$(0, 3^3, 0)$	485.2	−188.8	300.0	241.1
$(0, 3^1, 0)$	563.9	167.7	379.9	320.5
$(0, 4^4, 0)$	746.7	−289.8	465.8	269.8
$(0, 4^2, 0)$	811.3	116.6	540.3	421.9
$(0, 4^0, 0)$	838.9	333.6	571.5	491.8
$(1, 0^0, 0)$	1268.1	−380.2	1252.2	−244.2
$(0, 0^0, 1)$	3873.4	−127.7	2861.3	−21.6

[a] Determined using the $V + C$ anharmonic force field of Table 4.

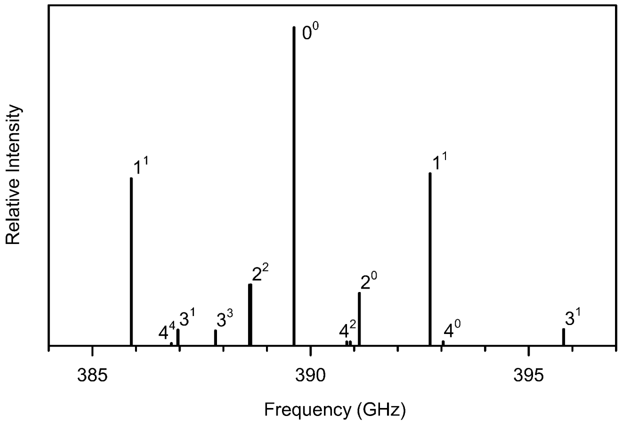

Figure 1. Stick diagram of the *a*-type $N = 5 \leftarrow 4$ rotational transitions of the main BeOH isotopomer arising from molecules in various bending energy levels. The lines are labeled with the $v_2^{l_2}$ quantum numbers, and spin splittings are not shown.

anharmonic force fields to be −21.8 and −22.0 cm^{-1}, respectively, compared to the observed shift[2] of −22.1 cm^{-1}.

The spin-averaged vibrational−rotational energy levels were further used to determine the effective rotational constant B_v for some excited vibrational states, especially those of the BeOH bending mode. The predicted term values and changes in the rotational constant B_v due to excitation of the vibrational modes of the BeOH and BeOD isotopic species are listed in Table 6. It is worth noting that these changes are quite large and very different for both isotopomers. For the BeOH isotopomer, the *l*-type doubling constant q_v is calculated to be 343.3 and 220.9 MHz for the $v_2^{l_2} = 1^1$ and 3^1 states, respectively. For the BeOD isotopomer, the corresponding constants q_v are determined to be 414.8 and 249.7 MHz. To illustrate the pattern of rotational transitions in the low-lying excited ν_2 states, Figure 1 shows a part of the predicted *a*-type $N = 5 \leftarrow 4$ rotational spectrum of the main BeOH isotopomer. The relative line intensities at 298 K were roughly estimated using formulas for a linear molecule.[28] The spin splittings are negligible on the scale of the Figure and therefore are not shown. Although some regularities can be found in the spectrum, the predicted pattern of rotational transitions in the excited ν_2 states resembles neither that characteristic of a linear molecule nor that of a well-bent molecule. The predicted pattern, however, is similar to that observed by Apponi et al.[29] in the rotational spectrum of the MgOD radical (see Figure 2 therein), and this molecule is known to be quasilinear.

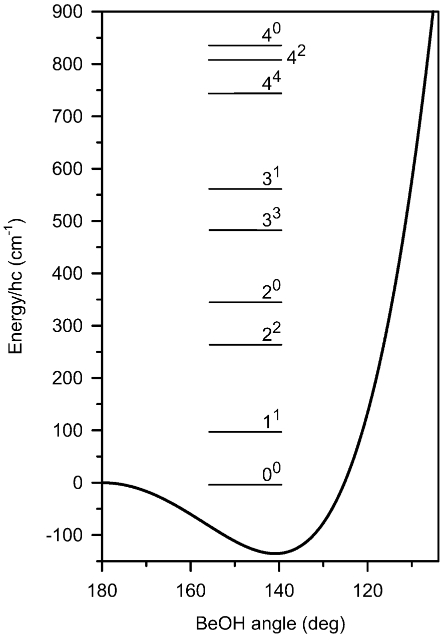

Figure 2. Minimum-energy potential function along the BeOH bending coordinate and location of the $v_2^{l_2}$ bending energy levels for the main BeOH isotopomer.

Figure 2 illustrates the predicted minimum-energy path along the BeOH bending coordinate q_3. Using the $V + C$ anharmonic force field of Table 4, the minimum-energy path $V_{mep}(q_3)$ was determined to be

$$V_{mep}(q_3) = -560q_3^2 + 518q_3^4 + 157q_3^6 - 68q_3^8 + 10q_3^{10} \quad (2)$$

where the potential energy and q_3 coordinate are given in wavenumbers and radians, respectively. The function $V_{mep}(q_3)$ is substantially different from a slice through the potential energy surface $V(q_1, q_2, q_3)$ for the BeO and OH bond lengths fixed at their equilibrium values

$$V(q_1 = 0, q_2 = 0, q_3) = -559q_3^2 + 952q_3^4 - 83q_3^6 - 8q_3^8 + 5q_3^{10} \quad (3)$$

The function $V(q_1 = 0, q_2 = 0, q_3)$ has a minimum at the valence BeOH angle of 148.3° with a barrier to linearity of 84 cm^{-1}. The difference between the functions $V_{mep}(q_3)$ and $V(q_1 = 0, q_2 = 0, q_3)$ is predominately due to a large change of the equilibrium BeO bond length along the minimum-energy path. This in turn is a result of strong anharmonic coupling between the BeO stretching and BeOH bending vibrations. Anharmonic coupling between the OH stretching and BeOH bending vibrations appears to be much weaker. For example (see Table 4), the expansion coefficient c_{104} is 2 orders of magnitude larger than c_{014}. By solving the 1D Schrödinger equation with the potential energy function $V_{mep}(q_3)$, the ground bending state of the main BeOH isotopomer was calculated to lie just 3 cm^{-1} below the top of the barrier to linearity. The classical turning points for this state are located at valence BeOH angles of 176 and 125°. The vibrational amplitude of the ν_2 mode of the main BeOH isotopomer in any of its energy levels thus amounts to more than 50°. Evidently, the BeOH bending mode can be called a large-amplitude motion, and the BeOH radical is shown to be another prominent example of a quasilinear molecule.

To quantify the quasilinearity of the BeOH radical, the parameter γ_0[30] can be calculated, ranging from −1 for an ideal linear molecule to +1 for an ideal bent molecule. From the

TABLE 7: Harmonic Wavenumbers ω_i and Anharmonic Constants x_{ij} (cm^{-1}) of X^{2}A′ BeOH and BeOD

	BeOH	BeOD
ω_1	1292.9	1273.2
ω_2	107.3	74.9
ω_3	4062.9	2960.2
x_{11}	−11.1	−11.0
x_{22}	17.8	11.1
x_{33}	−90.4	−49.0
x_{12}	−1.2	2.1
x_{13}	−2.9	−2.5
x_{23}	−7.2	0.2

calculated rotation−bending energy levels of the main BeOH isotopomer, the parameter γ_0 is determined to be −0.15. For a comparison, the parameter γ_0 is determined to be −0.74 and −1.05 for the MgOH and CaOH radicals, respectively.[13,14]

To estimate intensities of rotational transitions, the electric dipole moment of beryllium monohydroxide was calculated at the RCCSD(T)/cc-pV5Z level of theory using the finite field approach. For the equilibrium configuration, the dipole moment was determined to be 1.197 D, with the components parallel and perpendicular to the BeO bond being 0.605 and 1.033 D, respectively. Using the RHF wave function, the charge distributions were computed by the Mulliken population analysis to be $+0.41e$, $-0.70e$, and $+0.29e$ at the Be, O, and H atoms, respectively. At the linear configuration of the BeOH radical, the predicted dipole moment amounts to 1.241 D.

The vibrational energy levels of the BeOH radical can be further characterized by the harmonic frequencies ω_i and anharmonicity constants x_{ij}. The values predicted for the BeOH and BeOD isotopic species are given in Table 7. These were determined from the nine low-energy vibrational energy levels with $l_2 = 0$, including the fundamental, overtone, and combination levels. The vibrational constant g_{22} for the $v_2 = 2$ state is predicted to be quite large and negative, being −21.0 and −20.4 cm^{-1} for the BeOH and BeOD isotopomers, respectively. For the $v_2 = 4$ states of both isotopomers, the constants g_{22} are predicted to be smaller by a factor of ~2, the corresponding values being −8.1 and −8.9 cm^{-1}. Moreover, the l_2 dependence of the BeOH bending energy indicates a significant quartic contribution. For the $v_2 = 4$ state, the quartic term is determined here to be $0.1l^4$ cm^{-1}. Because the BeOH radical is considered in this study from a linear-molecule perspective, the predicted harmonic frequency for the BeOH bending mode, ω_2, is much lower than the 300−400 cm^{-1} found in previous theoretical studies.[2,4,6,9,10] However, in these studies, the harmonic frequency of the BeOH bending mode was determined for the BeOH radical treated as a bent molecule; therefore, it corresponds to the $v_2^{l_2} = 2^0$ energy level of a linear molecule. For the main BeOH isotopomer, the values calculated previously are consistent with the $v_2^{l_2} = 2^0$ term value of 348.4 cm^{-1} predicted in this study.

It is also interesting to address the question of the character of the ground-state electronic wave function for the BeOH radical. At the equilibrium configuration, the coupled-cluster $\mathcal{T}_1$ diagnostic[31] was determined to be 0.015, thus indicating weak nondynamical correlation effects. This was further confirmed by calculations using the internally contracted multireference configuration interaction (icMRCI) method[32,33] with the cc-pVQZ basis set. The reference wave function consisted of a full-valence complete active space (CAS). The wave function thus included all excitations of nine valence electrons in nine molecular orbitals corresponding to the valence atomic sp orbitals of the beryllium and oxygen atoms and the 1s orbital of the hydrogen atom. The multireference Davidson correction[34] to the calculated energy (icMRCI+Q) was employed to account for the effects of higher excitations approximately. The equilibrium structural parameters were calculated to be r(BeO) = 1.4022 Å, r(OH) = 0.9493 Å, and ∠(BeOH) = 139.01°. The barrier to linearity was determined to be 169 cm^{-1}. All of these values are essentially identical to those calculated at the RCCSD(T)/cc-pVQZ level of theory. The CI weight of the SCF configuration in the CASSCF wave function was found to be 0.959, whereas the weight of the reference wave function in the icMRCI wave function was 0.965. In conclusion, the nondynamical correlation effects appeared to be unimportant indeed, and the ground-state electronic wave function of the BeOH radical has essentially single-reference character.

Finally, other isomers of beryllium monohydroxide were considered, namely, HBeO and OHBe. At the icMRCI+Q/cc-pVQZ level of theory, both isomers were found to be linear at equilibrium, lying much higher in energy than X^{2}A′ BeOH. The relative energies of the X$^2\Sigma^+$ HBeO and OHBe isomers were calculated to be 63.5 and 128.7 kcal/mol, respectively. The calculated structure and energetics of the X$^2\Sigma^+$ HBeO radical are consistent with those determined in previous theoretical studies.[2,6,9]

We hope that the results reported in this study will stimulate further experimental work on beryllium monohydroxide and will be a useful guide for characterizing this interesting species by high-resolution vibrational−rotational spectroscopy.

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