Ab Initio Prediction of the Structure and Vibration−Rotation Spectroscopic Properties of Li_2OH and Li_2OH^+

Artur Gertych* and Jacek Koput

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60−780 Poznań, Poland

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The equilibrium structures and potential energy surfaces of the Li_2OH radical and the Li_2OH^+ cation in their ground electronic states have been determined from accurate ab initio calculations. The vibration−rotation energy levels and spectroscopic constants of three isotopic species (Li_2OH, Li_2OD, $^6Li_2OH$) were calculated by a perturbational approach. The predicted spectroscopic constants may serve as a useful guide for detecting these species by vibration−rotation spectroscopy and for assigning their spectra.

I. Introduction

Dilithium hydroxide, Li_2OH, is one of simplest examples of hypermetalated molecules.[1] The Li_2OH radical can be considered to result from reaction of a LiOH molecule with a Li atom. The extra Li atom is expected to bind to both O and Li atoms of LiOH. The isolated Li_2OH radical was predicted[1] to be thermodynamically stable. The experimental studies on dilithium hydroxide are very limited indeed. The first observation of the Li_2OH radical was made by Kudo et al.[2] in a supersonic beam by photoionization time-of-flight mass spectrometry. The adiabatic ionization energy of Li_2OH was then determined experimentally to be 4.053 eV.[3] To our knowledge, no information is available in the literature on spectroscopic properties of the Li_2OH radical and related species. Therefore, the structure and bonding of dilithium hydroxide is known only from theoretical sources. Schleyer[1] predicted the structure and dissociation energies of Li_2OH at the Hartree−Fock (HF) and Møller−Plesset second-order (MP2) levels of theory using the split-valence double-ζ (3-21G and 6-31G*) basis sets. The Li_2OH radical was found to have C_{2v} symmetry, with the LiO bond dissociation energy of about 40 kcal/mol. Kudo et al.[2−4] investigated the structure and energetics of various $Li_n(OH)_{n-1}$ ($n = 2-5$) clusters by the density functional theory (DFT), with the hybrid functional B3LYP, and by the MP2 approach using the split-valence triple-ζ basis set 6-311+G**. The ionization energies were determined at the B3LYP, MP2, and coupled-cluster CCSD(T) levels of theory. In particular, the adiabatic ionization energy of Li_2OH was predicted[4] to be 4.35, 4.03, and 4.07 eV by the B3LYP, MP2, and CCSD(T) methods, respectively. The structure and vibrational harmonic frequencies of the Li_2OH^+ cation were determined by Solomonik and Pogrebnaya[5] at the HF/DZP level. The Li_2OH^+ and Li_2OH^- ions were investigated by Nemukhin and Stepanov[6] at the HF and configuration−interaction CISD levels using the 6-31G basis set.

The present study was undertaken with the aim of predicting the structure and spectroscopic properties of dilithium hydroxide by the ab initio approach and of assisting future experimental studies. We present a detailed and accurate characterization of the potential energy surfaces and vibrational−rotational energy levels of dilithium hydroxide and its cation. The molecular parameters are determined using highly correlated wave functions, calculated with large correlation-consistent spdfgh basis sets, and taking into account core−electron correlation effects. We hope that the results reported here may serve as a useful guide for detecting dilithium hydroxide and related species by vibrational−rotational spectroscopy and for assigning their spectra.

II. Method of Calculation

The molecular parameters of the Li_2OH radical were calculated using the partially spin restricted open-shell coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T).[7−9] The coupled-cluster wave function was based on high-spin restricted Hartree−Fock (RHF) molecular orbitals as a reference function. Calculations for the Li_2OH^+ cation were performed using the closed-shell coupled-cluster method, CCSD(T).[10,11] The one-particle basis sets employed were the correlation-consistent polarized valence basis sets, cc-pV*n*Z.[12−14] The quality of the basis sets ranged from triple- to quintuple-ζ (n = T, Q, 5). The largest basis set, cc-pV5Z, consists of a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for lithium and oxygen and a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen. Only the spherical harmonic components of the d through h polarization functions were used. In the valence correlation treatment, the 1s-like core orbitals of the lithium and oxygen atoms were excluded from the active space. The core-related correlation effects were investigated using the correlation-consistent polarized core-valence basis set of triple- and quadruple-ζ quality, cc-pCVTZ, and cc-pCVQZ.[14,15] These basis sets are obtained by augmenting the corresponding standard cc-pV*n*Z basis sets with sets of tight functions. The largest basis set, cc-pCVQZ, is augmented with a (3s3p2d1f) set for lithium and oxygen, and it consists thus of a (15s9p5d3f1g)/[8s7p5d3f1g] set. The calculations were performed using the MOLPRO−2006 package of ab initio programs.[16]

Vibrational harmonic force fields of Li_2OH and Li_2OH^+ were calculated using the coupled-cluster methods, RCCSD(T) and CCSD(T), respectively. The anharmonic force fields of these species were determined using the spin unrestricted and restricted Møller−Plesset second-order methods, UMP2 and MP2, respectively.[17] These calculations were performed using the Gaussian 03 package of ab initio programs.[18] The spectro-

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* Corresponding author. E-mail: gertych@amu.edu.pl

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TABLE 1. Equilibrium Molecular Parameters of the X^2A_1 Li_2OH Radical and the X^1A_1 Li_2OH^+ Cation, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVTZ	cc-pVQZ	cc-pV5Z
	X^2A_1 Li_2OH		
r(LiO) (Å)	1.7495	1.7460	1.7461
r(OH) (Å)	0.9562	0.9544	0.9542
∠(LiOH) (deg)	132.29	132.25	132.31
Li•••Li[a] (Å)	2.5884	2.5848	2.5825
energy + 90 (hartree)	−0.721593	−0.748979	−0.757437
r(LiO)[b] (Å)	1.7553	1.7479	1.7468
r(OH)[b] (Å)	0.9573	0.9548	0.9544
∠(LiOH)[b] (deg)	132.59	132.37	132.35
Li•••Li[b] (Å)	2.5846	2.5827	2.5819
energy + 90[b] (hartree)	−0.727999	−0.751227	−0.758331
	X^1A_1 Li_2OH^+		
r(LiO) (Å)	1.7643	1.7583	1.7576
r(OH) (Å)	0.9623	0.9604	0.9602
∠(LiOH) (deg)	108.98	109.22	109.30
Li•••Li (Å)	3.3368	3.3206	3.3176
energy + 90 (hartree)	−0.573579	−0.600312	−0.608581
r(LiO)[b] (Å)	1.7656	1.7590	1.7579
r(OH)[b] (Å)	0.9632	0.9607	0.9603
∠(LiOH)[b] (deg)	109.04	109.31	109.31
Li•••Li[b] (Å)	3.3380	3.3201	3.3180
energy + 90[b] (hartree)	−0.579337	−0.602342	−0.609422

[a] The calculated distance between the Li atoms. [b] With the aug-cc-pV*n*Z basis set for oxygen.

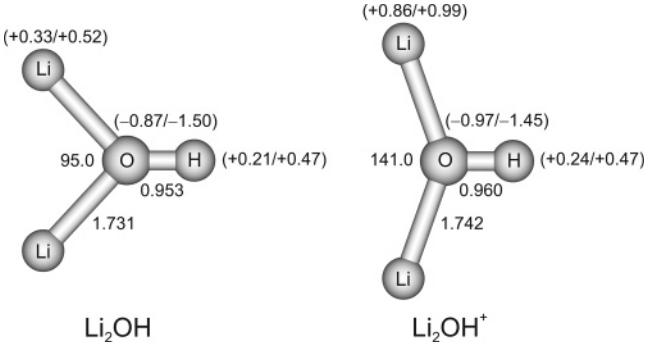

Figure 1. Predicted equilibrium structures of the ground electronic state of Li_2OH and Li_2OH^+. Bond lengths are given in Å and angles in degrees. Atomic charges, in *e*, determined by the Mulliken/NBO population analyses of the HF/cc-pCVQZ wave functions are given in parentheses.

TABLE 2. Equilibrium Molecular Parameters of the X^2A_1 Li_2OH Radical and the X^1A_1 Li_2OH^+ Cation, Determined Using the CCSD(T) Method with the cc-pCVTZ and cc-pCVQZ Basis Sets[a]

	V	*A*	*A* − *V*[b]
	X^2A_1 Li_2OH		
	cc-pCVTZ		
r(LiO) (Å)	1.7526	1.7399	−0.0127
r(OH) (Å)	0.9569	0.9562	−0.0007
∠(LiOH) (deg)	132.55	132.71	0.16
Li•••Li (Å)	2.5822	2.5569	−0.0253
energy (hartree)	−90.731823	−90.871586	−0.139763
	cc-pCVQZ		
r(LiO) (Å)	1.7472	1.7319	−0.0153
r(OH) (Å)	0.9550	0.9542	−0.0008
∠(LiOH) (deg)	132.38	132.50	0.12
Li•••Li (Å)	2.5813	2.5538	−0.0275
energy (hartree)	−90.752823	−90.902763	−0.149940
	X^1A_1 Li_2OH^+		
	cc-pCVTZ		
r(LiO) (Å)	1.7629	1.7504	−0.0125
r(OH) (Å)	0.9629	0.9623	−0.0006
∠(LiOH) (deg)	109.03	109.14	0.11
Li•••Li (Å)	3.3331	3.3073	−0.0258
energy (hartree)	−90.583150	−90.721747	−0.138597
	cc-pCVQZ		
r(LiO) (Å)	1.7584	1.7432	−0.0152
r(OH) (Å)	0.9608	0.9601	−0.0007
∠(LiOH) (deg)	109.31	109.47	0.16
Li•••Li (Å)	3.3190	3.2870	−0.0320
energy (hartree)	−90.603924	−90.752511	−0.148587

[a] With the aug-cc-pCV*n*Z basis set for oxygen. [b] A difference between the value determined correlating all of the electrons (*A*) and the value determined correlating only the valence electrons (*V*).

scopic constants were then determined using the second-order perturbational approach[19,20] as implemented in the Gaussian 03 package.

III. Results and Discussion

As expected from the previous studies,[1−4] the Li_2OH radical and the Li_2OH^+ cation were calculated to have a planar, Y-shaped equilibrium structure of C_{2v} symmetry. The ground electronic state of Li_2OH and Li_2OH^+ was found to be $^2A_1$ and $^1A_1$, respectively. The calculated structural parameters and total energies of both molecules are given in Table 1. The LiO bond lengths of Li_2OH and Li_2OH^+ are predicted here to be substantially shorter than those determined by Tanaka et al.[4] at the MP2/6-311+G(d,p) level of theory, being 1.758 and 1.770 Å, respectively; the OH bond length and the valence LiOH angle are quite alike. Following the Mulliken and natural-bond-orbital (NBO)[21] population analyses of the HF electron density, the LiO and OH bonds of Li_2OH and Li_2OH^+ are strongly polarized (see Figure 1 below), with a large negative charge of about −0.9*e* (Mulliken) and −1.5*e* (NBO) on the oxygen atom. To allow the one-particle basis set to adjust to such a charge distribution, we investigated the effects of diffuse functions. Additional calculations were performed with the augmented correlation-consistent basis sets aug-cc-pV*n*Z for oxygen,[22] and the results are also given in Table 1. For the largest basis set cc-pV5Z, enlargement of the basis set gives a negligible effect, the largest changes being observed for the LiO bond length and amounting to about 0.0005 Å. Although both lithium and hydrogen atoms have a single valence electron (2s and 1s, respectively), the LiO bond of Li_2OH and Li_2OH^+ is determined to be at equilibrium nearly twice as long as the OH bond.

As shown in Table 1 and Figure 1, ionization of the Li_2OH radical changes significantly its equilibrium structure. The LiO bonds lengthen by about 0.01 Å and the valence LiOLi angle increases from 95° for the neutral species to as much as 141° for the cation. This is consistent with the results of the Mulliken and NBO population analyses, which both indicate that the additional charge is localized on the lithium atoms. Upon ionization, the total charge of each Li atom of Li_2OH increases by about +0.5*e*, whereas the total charges of the oxygen and hydrogen atoms change by less than 0.1*e*. On the basis of a simple electrostatic model, the Li_2OH^+ cation can thus be expected to have a nearly T-shaped equilibrium structure. Apparently, the electrostatic interaction—Coulomb repulsion of the lithium atoms plays a dominant role in determining the shape of the Li_2OH^+ cation.

The effects of core−electron correlation on the molecular parameters of the Li_2OH radical and the Li_2OH^+ cation were investigated by comparing the values determined in calculations correlating only the valence electrons (*V*) with those when all of the electrons were correlated (*A*), both calculations performed with the same core-valence basis set. The results obtained with the cc-pCVTZ and cc-pCVQZ basis sets are given in Table 2.

Inclusion of the core-related effects substantially decreases the equilibrium LiO bond length. The $A - V$ change for the LiO bond is larger by a factor of ~20 than that for the OH bond.

The best estimate of the equilibrium structural parameters can be determined by adding the changes due to the core-related correlation $A - V$, determined with the cc-pCVQZ basis set, to the values determined with the largest valence basis set cc-pV5Z. For the Li_2OH radical, the equilibrium structural parameters are estimated in this way to be $r_e(\mathrm{LiO}) = 1.731$ Å, $r_e(\mathrm{OH}) = 0.953$ Å, and $\angle_e(\mathrm{LiOH}) = 132.5°$. For the Li_2OH^+ cation, the equilibrium structural parameters are $r_e(\mathrm{LiO}) = 1.742$ Å, $r_e(\mathrm{OH}) = 0.960$ Å, and $\angle_e(\mathrm{LiOH}) = 109.5°$. It is worth noting that the estimated values are equivalent to those computed with the cc-pCVQZ basis set while correlating all of the electrons. Considering convergence of the computed values with the one-particle basis set size and the effects of approximations inherent to the CCSD(T) approach, we estimate the uncertainty in the calculated bond lengths and angles to be about ±0.001 Å and ±0.1°, respectively. The predicted molecular parameters of the ground electronic state of Li_2OH and Li_2OH^+ are summarized in Figure 1. For both molecules, the predicted equilibrium LiO bond length is substantially longer than that found for dilithium oxide, Li_2O, determined experimentally[23] and theoretically[24] to be 1.611 and 1.616 Å, respectively. For lithium hydroxide, LiOH, the equilibrium LiO bond length was determined experimentally to be 1.5776 Å.[25] The predicted equilibrium OH bond length of Li_2OH and Li_2OH^+ is slightly longer than that of 0.949 Å found for LiOH.[25] The distance between the lithium atoms is predicted to be 2.552 and 3.284 Å for Li_2OH and Li_2OH^+, respectively. For the lithium dimer and its cation, Li_2 and Li_2^+, the bond length is calculated at the CCSD(T)/cc-pCVQZ level to be 2.6758 and 3.1010 Å, respectively, as compared with the experimental values[26,27] of 2.6730 and 3.12 Å. The predicted equilibrium structural parameters and atomic charge distribution suggest that the Li_2OH radical can be considered as two ionically bound units Li_2^+ and OH^-. However, because the Li···Li distance of Li_2OH is determined to be even shorter than that for the Li_2 molecule, there is strong Li−Li bonding enhanced by the OH^- moiety. This is similar to the bonding nature of dilithium oxide in its first singlet excited state $^1B_1$.[28] The Li_2O molecule was found both experimentally[28] and theoretically[29] to be strongly bent in the $^1B_1$ state, with the valence LiOLi angle of about 100°. On the other hand, the Li_2OH^+ cation can be considered as the OH^- group almost embedded in the Li_2^+[2] metallic "cluster".

To determine the shape of the potential energy surfaces of the Li_2OH radical and the Li_2OH^+ cation, the vibrational harmonic force fields and frequencies were calculated at various CCSD(T)/cc-pV*n*Z levels of theory. The results are given in Table 3. The 6 normal modes of the dilithium hydroxide molecule include 3 modes of A_1 symmetry ($\omega_1-\omega_3$), 1 mode of B_1 symmetry (ω_4), and 2 modes of B_2 symmetry (ω_5, ω_6), classified according to the C_{2v} symmetry group. The assignment of the vibrational modes is based on the potential energy distribution (PED). All of the normal vibrations of both species appear to be characteristic. Among the normal modes involving the lithium atoms, the higher energy mode has LiO stretching character, whereas the lower energy mode has LiOH bending character. It is worth noting that the assignment of the B_2 normal modes of the Li_2OH^+ cation is reversed. The effects of core−electron correlation on the harmonic frequencies are illustrated in Table 4. As could be expected, almost all of the harmonic frequencies of Li_2OH and Li_2OH^+ increase modestly upon inclusion of these effects. The changes due to the core-related correlation $A - V$, determined with the cc-pCVQZ basis set, were used to correct the harmonic frequencies determined in the valence-only calculations (Table 3). As for the equilibrium structural parameters, the corrected values appeared to be equivalent to those computed with the cc-pCVQZ basis set while correlating all of the electrons.

TABLE 3. Vibrational Harmonic Frequencies (in cm^{-1}) of the X^2A_1 Li_2OH Radical and the X^1A_1 Li_2OH^+ Cation, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets[a]

assignment	cc-pVTZ	cc-pVQZ	cc-pV5Z
	X^2A_1 Li_2OH		
ω_1 (OH stretch)	3911.6	3925.8	3929.0
ω_2 (sym LiO stretch)	685.4	693.3	694.2
ω_3 (sym LiOH bend)	270.9	270.3	270.3
ω_4 (out-of-plane)	282.3	277.2	277.3
ω_5 (asym LiO stretch)	649.9	659.8	660.7
ω_6 (asym LiOH bend)	510.4	518.4	519.2
	X^1A_1 Li_2OH^+		
ω_1 (OH stretch)	3830.9	3847.2	3850.4
ω_2 (sym LiO stretch)	615.2	624.2	625.0
ω_3 (sym LiOH bend)	224.1	225.3	225.5
ω_4 (out-of-plane)	345.8	346.9	347.0
ω_5 (asym LiOH bend)	798.4	802.8	803.6
ω_6 (asym LiO stretch)	726.8	734.6	736.0

[a] With the aug-cc-pV*n*Z basis set for oxygen.

TABLE 4. Vibrational Harmonic Frequencies (in cm^{-1}) of the X^2A_1 Li_2OH Radical and the X^1A_1 Li_2OH^+ Cation, Determined Using the CCSD(T) Method with the cc-pCVTZ and cc-pCVQZ Basis Sets[a]

	V	*A*	*A* − *V*[b]
		X^2A_1 Li_2OH	
		cc-pCVTZ	
ω_1	3904.8	3911.0	6.2
ω_2	684.9	693.5	8.6
ω_3	271.3	275.4	4.1
ω_4	280.9	287.2	6.3
ω_5	650.7	657.8	7.1
ω_6	509.5	507.2	−2.3
		cc-pCVQZ	
ω_1	3925.3	3932.0	6.7
ω_2	693.6	704.4	10.8
ω_3	270.4	275.2	4.8
ω_4	277.6	283.8	6.2
ω_5	660.3	669.6	9.3
ω_6	518.4	516.2	−2.2
		X^1A_1 Li_2OH^+	
		cc-pCVTZ	
ω_1	3824.9	3829.7	4.8
ω_2	615.1	622.2	7.1
ω_3	224.4	226.3	1.9
ω_4	346.5	350.7	4.2
ω_5	799.6	800.4	0.8
ω_6	726.6	734.1	7.5
		cc-pCVQZ	
ω_1	3846.8	3851.9	5.1
ω_2	624.5	634.0	9.5
ω_3	225.3	227.6	2.3
ω_4	346.9	350.9	4.0
ω_5	802.3	803.7	1.4
ω_6	735.0	744.8	9.8

[a] With the aug-cc-pCV*n*Z basis set for oxygen. [b] A difference between the value determined correlating all of the electrons (*A*) and the value determined correlating only the valence electrons (*V*).

The anharmonic force fields of the Li_2OH radical and the Li_2OH^+ cation were determined using the spin unrestricted and restricted Møller−Plesset second-order methods, respectively, in conjunction with the cc-pCVQZ basis set and correlating all

TABLE 5. Vibrational Harmonic (ω) and Fundamental (ν) Frequencies (in cm^{-1}) of the X^2A_1 Li_2OH Radical and the X^1A_1 Li_2OH^+ Cation, Determined at the MP2/cc-pCVQZ[a] Level of Theory

mode	ω	ν	$\nu - \omega$
	X^2A_1 Li_2OH		
1	3944.0 (0.2)[b]	3763.6	−180.4
2	694.5 (51)	671.7	−22.8
3	279.4 (14)	271.2	−8.2
4	287.9 (106)	288.4	0.5
5	660.3 (44)	634.1	−26.2
6	510.6 (11)	510.6	0.0
	X^1A_1 Li_2OH^+		
1	3862.5 (44)	3688.8	−173.7
2	623.8 (57)	608.8	−15.0
3	226.8 (135)	224.6	−2.2
4	350.6 (219)	352.4	1.8
5	801.7 (40)	794.2	−7.5
6	730.8 (328)	709.5	−21.3

[a] With the aug-cc-pCVQZ basis set for oxygen, all of the electrons correlated. [b] Infrared transition intensities are given in parenthesis, in km/mol.

TABLE 6. Predicted Vibrational Harmonic (ω) and Fundamental (ν) Frequencies (in cm^{-1}) of the Isotopomers Li_2OH, Li_2OD, and $^6Li_2OH$

	Li_2OH	Li_2OD	$^6Li_2OH$
ω_1	3936	2866	3936
ω_2	705	699	747
ω_3	275	274	293
ω_4	284	220	284
ω_5	670	644	704
ω_6	517	398	521
ν_1	3755	2770	3755
ν_2	682	676	722
ν_3	267	266	283
ν_4	284	220	285
ν_5	644	621	676
ν_6	517	397	521

of the electrons. For X^2A_1 Li_2OH, spin contamination of the UHF wave function appeared to be minimal indeed, with the total-spin-square (S^2) expectation value of 0.7503. The predicted harmonic (ω) and fundamental (ν) frequencies of both species are given in Table 5. The harmonic frequencies determined with the MP2 method differ from those determined with the CCSD(T) method by about 10 cm^{-1}. As shown by differences between the ω and ν values, the largest anharmonicity is observed for the OH stretching mode. Anharmonicity of the LiO stretching modes is significantly smaller, with the $\nu - \omega$ differences being by an order of magnitude smaller than that of the OH stretching mode.

Table 6 summarizes the vibrational constants—the harmonic and fundamental frequencies predicted for the three isotopomers of dilithium hydroxide, namely Li_2OH, Li_2OD, and $^6Li_2OH$. The predicted anharmonicity constants x of these species are given in Table S1 of the Supporting Information. The harmonic frequencies ω were calculated at the CCSD(T)/cc-pV5Z level of theory and corrected for the core−electron correlation effects determined at the CCSD(T)/cc-pCVQZ level. The anharmonicity corrections $\nu - \omega$, determined at the MP2/cc-pCVQZ level, were then added yielding the fundamental frequencies ν. For the main isotopic species Li_2OH, the harmonic and anharmonic zero-point energy (ZPE) is calculated to be 3191 and 3151 cm^{-1}, respectively. The vibrational constants predicted for the cations Li_2OH^+, Li_2OD^+, and $^6Li_2OH^+$ are given in Tables 7 and S2. For the main isotopic species Li_2OH^+, the harmonic and anharmonic ZPE is calculated to be 3306 and 3271 cm^{-1}, respectively. Considering convergence of the computed values with the one-particle basis set size and the effects of approximations inherent to the CCSD(T) and MP2 approaches, we estimate the uncertainty in the calculated frequencies to be about ±5 cm^{-1}.

TABLE 7. Predicted Vibrational Harmonic (ω) and Fundamental (ν) Frequencies (in cm^{-1}) of the Isotopomers Li_2OH^+, Li_2OD^+, and $^6Li_2OH^+$

	Li_2OH^+	Li_2OD^+	$^6Li_2OH^+$
ω_1	3856	2806	3856
ω_2	635	633	680
ω_3	228	226	240
ω_4	351	293	355
ω_5	805	746	812
ω_6	746	588	776
ν_1	3682	2714	3682
ν_2	620	618	663
ν_3	226	224	238
ν_4	353	294	357
ν_5	798	724	802
ν_6	725	583	755

TABLE 8. Predicted Equilibrium (B_e) and Ground-State Vibrationally Averaged (B_0) Rotational Constants, and Quartic Centrifugal Distortion Constants (in MHz) of the Isotopomers Li_2OH, Li_2OD, and $^6Li_2OH$

	Li_2OH	Li_2OD	$^6Li_2OH$
A_e	40 708	34 935	44 139
B_e	22 113	22 113	25 792
C_e	14 329	13 541	16 279
A_0	40 731	35 046	44 185
B_0	21 932	21 924	25 565
C_0	14 166	13 407	16 085
Δ_J	0.22	0.22	0.30
Δ_K	2.64	1.79	3.16
Δ_{JK}	−0.99	−0.85	−1.27
δ_J	0.09	0.10	0.13
δ_K	0.11	0.06	0.10

The predicted rotational and centrifugal distortion constants of the radicals Li_2OH, Li_2OD, and $^6Li_2OH$ are given in Table 8. The equilibrium rotational constants were calculated with the best estimates of the equilibrium structural parameters discussed above. The quartic centrifugal distortion constants were calculated for the A-reduction of the vibration−rotation Hamiltonian using the harmonic force field of dilithium hydroxide determined at the CCSD(T)/cc-pCVQZ level of theory. For the three isotopic species, the anharmonic vibration−rotation interaction constants α were determined at the MP2/cc-pCVQZ level, and their values are given in Table S3. The constants α were then used to calculate the ground-state vibrationally averaged rotational constants. The predicted rotational and centrifugal distortion constants of the cations Li_2OH^+, Li_2OD^+, and $^6Li_2OH^+$ are given in Table 9. It is worth noting that due to large structural changes upon ionization, the Li_2OH radical and the Li_2OH^+ cation are distinctly different asymmetric tops. The Li_2OH^+ cation is a nearly prolate symmetric top, with the asymmetry parameter $\kappa = -0.98$ (close to the limiting case of $\kappa = -1$). The Li_2OH radical is strongly asymmetric, with the asymmetry parameter $\kappa = -0.41$. Both species have thus qualitatively different patterns of the rotational energy levels and consequently qualitatively different rotational spectra. Uncertainties in the rotational constants can be estimated by varying the predicted equilibrium OH and LiO bond lengths and the LiOH angle within their estimated error bars of ±0.001 Å and ±0.1°, respectively. For the main isotopic species Li_2OH, varying the OH bond length results in a small change of the constant A of ∓10 MHz, whereas it does not affect the constants B and C. Upon varying the LiO bond length, the constants A, B, and C change by ∓40, ∓25, and ∓15 MHz,

TABLE 9. Predicted Equilibrium (B_e) and Ground-state Vibrationally Averaged (B_0) Rotational Constants, and Quartic Centrifugal Distortion Constants (in MHz) of the Isotopomers Li_2OH^+, Li_2OD^+, and $^6Li_2OH^+$

	Li_2OH^+	Li_2OD^+	$^6Li_2OH^+$
A_e	126 130	93 743	134 945
B_e	13 357	13 357	15 579
C_e	12 078	11 691	13 967
A_0	129 032	95 310	138 102
B_0	13 284	13 288	15 490
C_0	11 977	11 598	13 843
Δ_J	0.05	0.04	0.06
Δ_K	109.36	41.21	120.48
Δ_{JK}	−2.33	−1.26	−2.73
δ_J	0.01	0.01	0.01
δ_K	0.26	0.23	0.33

respectively. Upon varying the LiOH angle, the constants A, B, and C change by ∓ 140, ± 70, and ± 10 MHz, respectively.

To estimate intensities of the rotational transitions, the electric dipole moment of the Li_2OH radical was calculated by the finite-field approach at the RCCSD(T)/cc-pCVQZ level with all of the electrons correlated. For the equilibrium configuration, the total dipole moment of Li_2OH was found to be 2.34 D.

Finally, to assess quality of the calculated electronic structure of dilithium hydroxide, the adiabatic ionization energy of the Li_2OH radical was determined. The total energy difference between the equilibrium configurations of Li_2OH and Li_2OH^+ is calculated with the CCSD(T) method to be 4.0453, 4.0514, and 4.0520 eV for the cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets, respectively. Inclusion of the core−electron correlation effects increases the total energy difference by 0.0317 and 0.0368 eV, as calculated with the CCSD(T) method in conjunction with the cc-pCVTZ and cc-pCVQZ basis set, respectively. Inclusion of the vibrational zero-point energies of both species increases further the total energy difference by 0.0143 and 0.0149 eV within the harmonic and anharmonic approximation, respectively. The best theoretical estimate of the adiabatic ionization energy of the Li_2OH radical is thus obtained to be 4.104 eV, as compared with the experimental value of 4.053 eV.[3]

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Supporting Information Available: The vibrational anharmonicity constants x and vibration−rotation interaction constants α for the three isotopic species Li_2OH, Li_2OD, and $^6Li_2OH$, and for the corresponding cations are given in Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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