

# The *ab initio* potential energy surface and vibrational-rotational energy levels of $X^2\Sigma^+ \text{MgOH}$

Jacek Koput<sup>a)</sup>

Department of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland

Stuart Carter

Department of Chemistry, University of Reading, Reading RG6 2AD, United Kingdom

Kirk A. Peterson

Department of Chemistry, Washington State University, Richland, Washington and Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352

Giannoula Theodorakopoulos

Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, Athens 11635, Greece

(Received 7 February 2002; accepted 23 April 2002)

The equilibrium structure and potential energy surface of magnesium monohydroxide in its ground doublet state,  $X^2\Sigma^+ \text{MgOH}$ , 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-zeta quality. The effects of core-electron correlation on the calculated molecular parameters were investigated. The vibrational-rotational energy levels of various MgOH isotopomers were calculated using the variational method. The spectroscopic constants determined are found to be in remarkably good agreement with experimental data. © 2002 American Institute of Physics.  
[DOI: 10.1063/1.1485721]

## I. INTRODUCTION

Alkaline-earth monohydroxides, MOH, are of interest because of the different nature of M–OH bonding depending on whether the metal atom M is beryllium (Be), magnesium (Mg), or calcium (Ca). In the early experimental and theoretical studies,<sup>1–4</sup> the CaOH molecule was found to be linear at equilibrium, with the bending potential energy function being nearly harmonic. This is consistent with ionic bonding, with the charge distribution closely resembling  $\text{M}^+\text{OH}^-$ . On the other hand, the BeOH molecule was predicted<sup>3,4</sup> to be bent at equilibrium, with a valence angle BeOH of about  $150^\circ$  and a small barrier to linearity of only about  $50 \text{ cm}^{-1}$ . This in turn indicates a strong admixture of covalent bonding. The bending potential energy function for the MgOH molecule was determined<sup>2–4</sup> to be intermediate between those for the CaOH and BeOH molecules. Magnesium hydroxide was found to have a linear equilibrium configuration, however, with the flat, essentially quartic MgOH bending potential energy function. As a result, the MgOH molecule was concluded<sup>2</sup> to be quasilinear.

The further experimental evidence for quasilinearity of magnesium monohydroxide came from high-resolution spectroscopic studies.<sup>5–9</sup> The pure rotational spectra of the MgOH and MgOD isotopomers were measured in the ground state and excited states of the MgOH/MgOD bending mode  $\nu_2$ . The dependence of the effective rotational constant  $B_v$  on the quantum numbers  $\nu_2$  and  $l_2$  was found to be highly nonlinear for both molecules.<sup>7,9</sup> Additionally, some

MgOH/MgOD bending vibrational energies and the MgO stretching frequency ( $\nu_1$  mode) were determined by laser-induced fluorescence.<sup>2,7</sup> All of these data were analyzed by Bunker *et al.*<sup>7</sup> with the six-dimensional vibrational-rotational Hamiltonian. By using the results of calculations at the MP2/6-31++G\*\* level of theory and adjusting some expansion coefficients, the combined *ab initio*/empirical anharmonic force field of magnesium monohydroxide was determined. In particular, the bending potential energy function was found to be dominated by a quartic contribution. To our knowledge, this is the most accurate anharmonic force field of magnesium monohydroxide available to date in the literature.

In this study, we present a detailed and accurate characterization of the potential energy surface and vibrational-rotational energy levels of magnesium 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.

## II. METHOD OF CALCULATION

The molecular parameters of magnesium 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),<sup>10–12</sup> based on spin-restricted Hartree–Fock (RHF) molecular orbitals as a reference wave function. The one-particle basis sets employed were the correlation-consistent polarized valence basis sets, cc-pVnZ.<sup>13,14</sup> The

<sup>a)</sup>Electronic mail: koput@amu.edu.pl

TABLE I. The equilibrium molecular parameters of  $X^2\Sigma^+$  MgOH, determined using the RCCSD(T) method and various cc-pVnZ basis sets.

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
$r(\text{MgO})$ (Å)	1.7789	1.7749	1.7745	1.7742
$r(\text{OH})$ (Å)	0.9549	0.9481	0.9467	0.9468
Energy + 275 (hartree)	-0.298 128	-0.396 721	-0.427 767	-0.438 286

quality of the basis sets ranged from double-zeta ( $n=D$ ), through triple- ( $n=T$ ) and quadruple-zeta ( $n=Q$ ), to quintuple-zeta ( $n=5$ ). The cc-pVnZ basis sets provide a systematic way of enlarging the basis set. The accuracy of the results obtained with increasing quality of the one-particle basis set can be conveniently estimated by assuming monotonic convergence of the calculated properties towards the limit of an infinite basis set. The largest basis set, cc-pV5Z, consists of a  $(20s14p4d3f2g1h)/[7s6p4d3f2g1h]$  set for magnesium,  $(14s8p4d3f2g1h)/[6s5p4d3f2g1h]$  set for oxygen, and a  $(8s4p3d2f1g)/[5s4p3d2f1g]$  set for hydrogen. Only the spherical harmonic components of the  $d$  through  $h$  polarization functions were used. In the correlation treatment, the  $1s2sp$ - and  $1s$ -like core orbitals of the magnesium and oxygen atoms, respectively, were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent polarized core-valence basis sets of triple- and quadruple-zeta quality, cc-pCVTZ and cc-pCVQZ.<sup>14,15</sup> These basis sets are obtained by augmenting the corresponding standard cc-pVnZ basis sets with sets of tight functions. The largest basis set, cc-pCVQZ, is augmented with a  $(3s3p3d2f1g)$  set for magnesium and a  $(3s3p2d1f)$  set for oxygen. It consists thus of a  $(19s15p6d4f2g)/[9s8p6d4f2g]$  set for magnesium,  $(15s9p5d3f1g)/[8s7p5d3f1g]$  set for oxygen, and a  $(6s3p2d1f)/[4s3p2d1f]$  set for hydrogen. In the correlation treatment involving the core and valence electrons, only the  $1s$ -like core orbital of the magnesium atom was excluded from the active space.

The calculations were performed using the MOLPRO-2000 package of *ab initio* programs.<sup>16</sup>

The vibrational-rotational energy levels were calculated variationally using the six-dimensional Hamiltonian of a triatomic molecule.<sup>17-20</sup> The Hamiltonian, including the exact kinetic energy operator, was derived in terms of the internal

valence coordinates. The initial vibrational basis set consisted of harmonic oscillator functions for the stretching coordinates and of associated Legendre functions for the bending coordinate. Expansion functions were constructed as contracted combinations of the initial basis set functions. For the stretching part, the one-dimensional expansion functions were optimized to yield contracted two-dimensional stretching functions. Vibrational basis set functions were then formed as products of the contracted two-dimensional stretching functions and one-dimensional 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 two-dimensional stretching functions was 40, and the number of contracted bending functions was 20, leading to a total of 800 vibrational basis functions. This size of the basis set ensured the convergence in the energy to within  $\approx 10^{-6}$  cm<sup>-1</sup> for the vibrational-rotational energy levels under interest.

### III. RESULTS AND DISCUSSION

In the previous theoretical studies,<sup>3,4,21-23</sup> the MgOH radical was found to be linear at equilibrium in the ground electronic state, being of  $\Sigma^+$  symmetry in the  $C_{\infty v}$  point group. The equilibrium bond lengths and total energy computed here by the RCCSD(T) approach are listed in Table I. It is worth noting that the calculated MgO bond length only slightly depends on the quality of the one-particle basis set. On going from the cc-pVDZ to cc-pV5Z basis set, the MgO bond length decreases by only 0.0047 Å, as compared with

TABLE II. The equilibrium molecular parameters of  $X^2\Sigma^+$  MgOH, determined using the RCCSD(T) method with the cc-pCVTZ and cc-pCVQZ basis sets.

	Valence-only (V) <sup>a</sup>	All-electrons (A) <sup>b</sup>	A - V
cc-pCVTZ			
$r(\text{MgO})$ (Å)	1.7683	1.7607	-0.0076
$r(\text{OH})$ (Å)	0.9476	0.9471	-0.0005
Energy (hartree)	-275.401 512	-275.725 937	-0.324 425
cc-pCVQZ			
$r(\text{MgO})$ (Å)	1.7702	1.7592	-0.0110
$r(\text{OH})$ (Å)	0.9468	0.9461	-0.0007
Energy (hartree)	-275.430 165	-275.794 981	-0.364 816

<sup>a</sup>Correlating only the valence electrons.

<sup>b</sup>Correlating all of the electrons, except the  $1s$  electrons of the magnesium atom.

the analogous change of the OH bond length of 0.0081 Å. Changes in the calculated bond lengths beyond the cc-pV5Z basis set can be expected to be negligibly small. Analogous changes in the total energy were estimated applying the exponential/Gaussian extrapolation formula.<sup>24</sup> Extension from the cc-pV5Z to cc-pV6Z basis set would lower the total energy by  $\approx 4$  mhartrees, while the total energy lowering at the limit of the infinite basis set could be estimated to be  $\approx 6$  mhartrees.

The effects of core-electron correlation on the molecular parameters were investigated by comparing the values determined in calculations involving only the valence electrons with those when the valence and core electrons were correlated, both calculations 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 II. Inclusion of the core-related effects substantially decreases the equilibrium MgO bond length, whereas the OH bond length is only slightly effected. In this context, it is worth noting that the magnesium  $2sp$ -like orbitals are not really the core orbitals in the same way as the oxygen  $1s$ -like orbital. For the MgOH radical, the energies of the magnesium  $2sp$ -like orbitals range from  $-3.8$  to  $-2.3$  hartrees, whereas the energy of the oxygen  $1s$ -like orbital is  $-20.5$  hartrees. Therefore, efficient mixing of the magnesium  $2sp$  and oxygen valence orbitals may occur. Especially important mixing may occur between the magnesium  $2p_z$  and oxygen  $2s$  orbitals, both contributing to the single (sigma) MgO bond. This effect has been found to be rather large for calcium-containing molecules and will be discussed in detail elsewhere.<sup>25</sup> However, for the MgOH radical, the Hartree-Fock molecular orbitals corresponding to the magnesium  $2p_z$  and oxygen  $2s$  orbitals are found to be quite localized. By using the cc-pV5Z basis set and localizing these orbitals according to the Boys criterion,<sup>26</sup> the equilibrium bond lengths are determined at the RCCSD(T) level of theory to be  $r(\text{MgO}) = 1.7737$  Å and  $r(\text{OH}) = 0.9468$  Å, with the total energy being  $-275.438317$  hartrees. These values are essentially identical with those quoted in Table I, lending thus plausibility to the “valence” description of magnesium monohydroxide.

The best estimate of the equilibrium bond lengths can be determined by adding the “ $A - V$ ” changes obtained with the cc-pCVQZ basis set to the corresponding values obtained with the cc-pV5Z basis set. The equilibrium bond lengths of magnesium monohydroxide are thus estimated to be  $r_e(\text{MgO}) = 1.763$  Å and  $r_e(\text{OH}) = 0.946$  Å. 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 uncertainty in the calculated bond lengths to be about  $\pm 0.001$  Å. In comparison, the equilibrium MgO bond length has been determined at various other levels of theory to be 1.758 Å at the CISD/TZ4P level,<sup>4</sup> 1.802 Å at the CASSCF/TZ4P level,<sup>21</sup> and 1.731 Å at the MP2/6-311++G\*\* level.<sup>23</sup> The equilibrium MgO bond length was determined experimentally to be 1.761 (Ref. 7) and 1.767 Å.<sup>9</sup> The latter value is likely overestimated, as the zero-point averaging effects of the MgO and OH stretching vibrations were not taken into account.<sup>9</sup> The

TABLE III. The anharmonic force field [the expansion coefficients  $c_{ijk}$  of Eq. (1), in hartrees]<sup>a</sup> of  $X^2\Sigma^+$  MgOH.

$i$	$j$	$k$	$V^b$	$V+C^c$
0	0	2	0.000 186	0.000 366
2	0	0	1.237 443	1.244 429
0	2	0	0.942 430	0.943 232
0	0	4	0.002 979	0.002 799
1	1	0	-0.016 580	-0.015 896
1	0	2	-0.093 489	-0.095 349
0	1	2	-0.017 576	-0.017 446
3	0	0	-1.233 314	-1.216 901
0	3	0	-0.175 624	-0.176 005
0	0	6	-0.000 442	-0.000 353
1	2	0	-0.015 305	-0.014 106
1	0	4	0.028 477	0.029 479
0	1	4	0.001 460	0.001 385
2	1	0	-0.093 436	-0.092 305
2	0	2	0.055 655	0.055 566
0	2	2	-0.021 397	-0.021 467
1	1	2	-0.010 314	-0.011 556
4	0	0	-0.005 992	-0.023 818
0	4	0	-0.354 386	-0.354 565
0	0	8	0.000 100	0.000 078
1	3	0	-0.047 194	-0.043 325
1	0	6	-0.005 046	-0.005 357
0	1	6	-0.001 151	-0.001 148
3	1	0	0.091 894	0.100 852
3	0	2	-0.025 172	-0.027 967
0	3	2	-0.015 048	-0.014 763
2	2	0	-0.166 299	-0.169 325
2	0	4	-0.004 301	-0.002 439
0	2	4	0.002 265	0.002 582
1	1	4	0.021 479	0.022 930
1	2	2	-0.029 333	-0.030 220
2	1	2	0.029 032	0.026 245
5	0	0	0.458 043	0.321 457
0	5	0	-0.309 585	-0.308 433
0	0	10	-0.000 002	-0.000 001
1	4	0	-0.057 040	-0.053 590
1	0	8	0.000 280	0.000 360
0	1	8	0.000 280	0.000 288
4	1	0	-0.102 412	-0.147 259
4	0	2	0.004 404	-0.011 832
0	4	2	0.017 418	0.017 632
2	3	0	-0.116 107	-0.125 207
2	0	6	-0.003 919	-0.004 964
0	2	6	-0.001 349	-0.001 473
3	2	0	0.063 964	0.064 259
3	0	4	0.013 975	0.017 191
0	3	4	0.000 204	0.000 280
1	1	6	-0.004 629	-0.005 177
1	3	2	0.004 430	0.002 853
3	1	2	-0.059 096	-0.057 015
1	2	4	0.021 112	0.021 152
2	1	4	0.005 791	0.007 362
2	2	2	0.063 048	0.065 505

<sup>a</sup>The coordinates  $q_1$  and  $q_2$  are dimensionless,  $q_3$  is in radians.

<sup>b</sup>Determined at the RCCSD(T)/cc-pV5Z level of theory.

<sup>c</sup>Including corrections for the core-electron correlation effects determined at the RCCSD(T)/cc-pCVQZ level.

equilibrium MgO bond length estimated here at the RCCSD(T) level of theory is just midway between the two experimental values quoted. The equilibrium OH bond length was predicted to be 0.951 Å at the CASSCF/TZ4P level<sup>21</sup> and 0.952 Å at the MP2/6-311++G\*\* level.<sup>23</sup> The

TABLE IV. The fundamental vibrational wave numbers (in  $\text{cm}^{-1}$ ) of  $X^2\Sigma^+$  MgOH and MgOD.

Assignment	MgOH			MgOD		
	$V^a$	$V+C^a$	Expt. <sup>b</sup>	$V^a$	$V+C^a$	Expt. <sup>b</sup>
$\nu_1$ (MgO stretch)	740	747	750	725	732	
$\nu_2$ (MgOH bend)	157	160	161	107	109	109
$\nu_3$ (OH stretch)	3845	3851		2842	2846	
ZPE <sup>c</sup>	2490	2502		1912	1923	

<sup>a</sup>Determined using the corresponding anharmonic force field of Table III.

<sup>b</sup>From Refs. 2 and 7.

<sup>c</sup>The zero-point energy.

value of 0.946 Å predicted in this work is similar and somewhat closer to the experimental estimate of 0.940 Å.<sup>9</sup> However, the experimental estimate of the equilibrium OH bond length may be quite inaccurate due to the unusually large zero-point averaging effect of the MgOH bending vibration (the quasilinearity effect).

Concerning the equilibrium structure of magnesium monohydroxide, it is also worth noting that in recent calculations using density functional theory (DFT),<sup>23,27</sup> the MgOH radical is erroneously predicted to be bent in the ground electronic state.

To determine the shape of the potential energy surface of magnesium monohydroxide, the total energy was calculated at 215 points in the vicinity of the equilibrium configuration, with the energies ranging to approximately 11 000  $\text{cm}^{-1}$  above the minimum. The energies were determined at the RCCSD(T)/cc-pV5Z level of theory, with an accuracy better than  $10^{-8}$  hartrees. The potential energy surface was then approximated by a three-dimensional expansion along the internal valence coordinates. The internal coordinates for the MgO and OH stretching modes were chosen as Simons–Parr–Finlan coordinates,<sup>28</sup>  $q = (r - r_e)/r$ , where  $r$  and  $r_e$  are instantaneous and equilibrium bond lengths, respectively. For the MgOH bending mode, a curvilinear displacement coordinate was used,<sup>29</sup> defined as the supplement of the valence angle MgOH. The coordinates for the MgO and OH stretching modes are referred to hereafter as  $q_1$  and  $q_2$ , respectively, whereas that for the MgOH bending mode as  $q_3$ . Thus, the potential energy surface of magnesium monohydroxide can be written as the polynomial expansion,

$$V(q_1, q_2, q_3) = V_m + \sum_{ijk} c_{ijk} q_1^i q_2^j q_3^k, \quad (1)$$

where  $V_m$  is the total energy at the minimum. The expansion coefficients  $c_{ijk}$  were determined from a least-squares fit of Eq. (1) to the computed total energies, and 53 coefficients appeared to be statistically significant. The optimized values of the expansion coefficients are listed in Table III under the column headed “ $V$ .” Note that due to symmetry of the MgOH molecule, the exponent  $k$  (for the MgOH bending mode) takes only even values. The root-mean-square deviation of the fit was about 4.1  $\mu$ hartrees (0.9  $\text{cm}^{-1}$ ).

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 magnesium monohydroxide was

computed at the same points as calculated previously, correlating either only valence or valence and core electrons. At each point, a 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). The optimized values of the expansion coefficients  $c_{ijk}$  are listed in Table III under the column headed “ $V+C$ .”

The accuracy of the calculated potential energy surfaces can easily be assessed by comparing the calculated spin-averaged vibrational-rotational energy levels with those determined experimentally. The fundamental vibrational frequencies for the two isotopic species, MgOH and MgOD, are given in Table IV. To our knowledge, the only available experimental data in the literature are the fundamental MgO stretching frequency of MgOH and the MgOH and MgOD bending frequencies.<sup>2,7</sup> The experimental vibrational wave numbers are estimated<sup>7</sup> to be accurate to about  $\pm 3 \text{ cm}^{-1}$ . The fundamental wave numbers predicted with the “ $V+C$ ” anharmonic force field coincide with the experimental values to within the error bars. The fundamental vibrational wave numbers predicted with the “ $V$ ” force field are lower by 2–7  $\text{cm}^{-1}$  than those predicted with the “ $V+C$ ” force field. For the MgOH isotopomer, the fundamental OH stretching wave number was predicted by Bunker *et al.*<sup>7</sup> to be 3214  $\text{cm}^{-1}$ . The value predicted in this work, of 3851  $\text{cm}^{-1}$ , is more than 600  $\text{cm}^{-1}$  higher. Since for magnesium monohydroxide the charge distribution resembles the structure  $\text{Mg}^+\text{OH}^-$ , the fundamental OH stretching frequency can be expected to be close to that of the  $\text{OH}^-$  anion or the OH radical. These fundamental wave numbers are observed experimentally<sup>30,31</sup> to be about 3600  $\text{cm}^{-1}$ . Moreover, the harmonic OH stretching wave number for the MgOH isotopomer is predicted to

TABLE V. The ground-state effective rotational constant  $B_0$  (in MHz) of various MgOH isotopomers.

	$V^a$	$V+C^a$	Expt. <sup>b</sup>
MgOH	14 601	14 775	14 822.516
MgOD	13 248	13 399	13 438.500
<sup>26</sup> MgOH	14 147	14 315	14 361.137
<sup>25</sup> MgOH	14 365	14 535	14 581.799

<sup>a</sup>Determined using the corresponding anharmonic force field of Table III.

<sup>b</sup>From Refs. 5 and 8.

TABLE VI. The observed and calculated vibrational energy differences (in  $\text{cm}^{-1}$ ) of  $X^2\Sigma^+$  MgOH and MgOD.

Energy	Obs. <sup>a</sup>	Calc. <sup>b</sup>
MgOH		
$E(1,0^0,0)^c$	750	747
$E(0,2^0,0)^c$	375	369
$E(0,4^0,0)^c$	862	856
$E(0,6^0,0)^c$	1430	1420
$E(0,8^0,0)^c$	2041	2035
$E(0,3^1,0)^d$	441	442
$E(0,5^1,0)^d$	974	973
$E(0,7^1,0)^d$	1564	1566
$E(0,9^1,0)^d$	2199	2199
MgOD		
$E(0,2^0,0)^c$	260	255
$E(0,4^0,0)^c$	597	592
$E(0,6^0,0)^c$	1002	989
$E(0,8^0,0)^c$	1436	1420
$E(0,10^0,0)^c$	1896	1890
$E(0,12^0,0)^c$	2397	2391
$E(0,14^0,0)^c$	2920	2919
$E(0,3^1,0)^d$	309	305
$E(0,5^1,0)^d$	685	672
$E(0,7^1,0)^d$	1101	1090
$E(0,9^1,0)^d$	1546	1543
$E(0,11^1,0)^d$	2033	2030

<sup>a</sup>From Ref. 7.<sup>b</sup>Determined using the  $V+C$  anharmonic force field of Table III.<sup>c</sup>Relative to the  $(0,0^0,0)$  energy level.<sup>d</sup>Relative to the  $(0,1^1,0)$  energy level.

be  $4012\text{ cm}^{-1}$  at the CASSCF/TZ4P level<sup>21</sup> and  $4085\text{ cm}^{-1}$  at the MP2/6-311+G\*\* level.<sup>23</sup> Therefore, the fundamental OH stretching wave number predicted previously with the combined *ab initio*/empirical anharmonic force field<sup>7</sup> is likely erroneous.

Table V lists values of the ground-state effective rotational constant,  $B_0$ , calculated for various MgOH isotopomers. The predicted rotational constants consistently underestimate the experimental values, by about 200 and 50 MHz for the “ $V$ ” and “ $V+C$ ” anharmonic force field, respectively. Inclusion of the core-electron correlation effects significantly improves agreement with the experimental data

and, therefore, only the results obtained with the  $V+C$  anharmonic force field will be further discussed.

A comparison of the observed and calculated vibrational energy levels of the MgOH and MgOD isotopomers is presented in Table VI. Agreement between the observed and calculated energy levels is remarkably good, with the root-mean-square deviation being only 5.0 and  $8.5\text{ cm}^{-1}$  for MgOH and MgOD, respectively. In fact, it is of nearly the same quality as that obtained using the optimized parameters of the combined *ab initio*/empirical anharmonic force field.<sup>7</sup>

Table VII lists the predicted  $N=l_2$  term values and changes in the effective rotational constant,  $\Delta B_v$ , for the low-lying energy levels of the MgOH and MgOD isotopomers. It is worth noting that these changes are quite large and very different for both the isotopomers. A comparison with the experimental data<sup>5,8,9</sup> shows that the changes in the rotational constant  $B_v$  due to excitation of the MgOH bending mode ( $\nu_2$ ) are predicted to high accuracy. Except for the  $\nu_2^1=4^2$  state of MgOH, the changes  $\Delta B_v$  are reproduced to better than  $\pm 2$  MHz. The predicted change  $\Delta B_v$  for the  $4^2$  state is off from the experimental value by 26 MHz, and the reason for this apparent discrepancy is not known. For the MgOH isotopomer, the  $l$ -type doubling constant  $q$  is calculated to be 84.6 and 65.2 MHz for the  $\nu_2^1=1^1$  and  $3^1$  states, respectively, as compared with the experimental values<sup>9</sup> of 85.13 and 65.86 MHz, respectively. For the MgOD isotopomer, the corresponding constants are predicted to be 100.3 and 77.7 MHz, as compared with the experimental values<sup>9</sup> of 100.89 and 78.27 MHz, respectively. For both the isotopomers, the predicted patterns of rotational transitions in the excited  $\nu_2$  states agree thus very favorably with the experimental data. In particular, the anomalous qualitative difference between the rotational spectra of the MgOH and MgOD radicals is nicely predicted. It is also interesting to note that using the combined *ab initio*/empirical anharmonic force field,<sup>7</sup> the changes  $\Delta B_v$  due to excitation of the  $\nu_2$  mode were reproduced to within only about  $\pm 5$  MHz.

The changes  $\Delta B_v$  can further be characterized by the rotation-vibration interaction constants  $\alpha_i$ . For the MgO and OH stretching modes,  $\nu_1$  and  $\nu_3$ , a conventional linear de-

TABLE VII. The  $J=l_2$  vibrational-rotational term values (in  $\text{cm}^{-1}$ ) and changes in the effective rotational constant  $B_v$  (in MHz) for the low-lying energy levels of  $X^2\Sigma^+$  MgOH and MgOD.

$(v_1, \nu_2^l, v_3)$	MgOH			MgOD		
	Energy/ $hc^a$	$\Delta B_v$ (calc.) <sup>a</sup>	$\Delta B_v$ (obs.) <sup>b</sup>	Energy/ $hc^a$	$\Delta B_v$ (calc.) <sup>a</sup>	$\Delta B_v$ (obs.) <sup>b</sup>
$(0,0^0,0)$	0	0	0	0	0	0
$(0,1^1,0)$	159.9	-65.9	-65.335	109.1	7.0	7.904
$(0,2^0,0)$	368.6	-51.6	-51.498	254.6	43.8	44.935
$(0,2^2,0)$	362.1	-125.3	-124.478	244.3	4.6	6.186
$(0,3^1,0)$	601.4	-78.2	-77.806	414.0	58.7	60.265
$(0,3^3,0)$	601.7	-179.1	-178.145	402.0	-1.5	0.508
$(0,4^0,0)$	856.2	-71.7		591.7	92.2	
$(0,4^2,0)$	861.5	-116.6	-142.580	589.2	61.9	
$(0,4^4,0)$	876.0	-227.8		580.2	-10.4	-8.304
$(1,0^0,0)$	747.0	-122.1		731.6	-100.6	
$(0,0^0,1)$	3850.5	-59.5		2846.2	-46.6	

<sup>a</sup>Determined using the  $V+C$  anharmonic force field of Table III.<sup>b</sup>From Refs. 5, 8, 9.

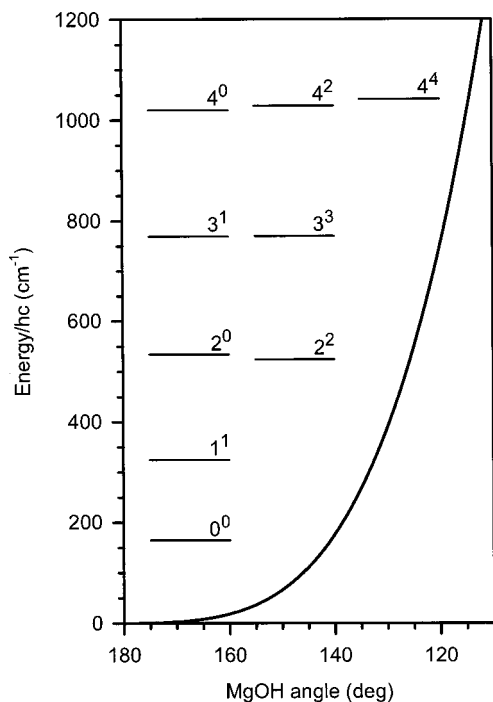


FIG. 1. The MgOH bending potential energy function and location of the  $v_2^{l_2}$  bending energy levels for the main MgOH isotopomer.

pendence with respect to the quantum numbers  $v_1$  and  $v_3$  can be assumed. As shown in Table VII, this leads to the constants  $\alpha_1 = 122.1$  and  $\alpha_3 = 59.5$  MHz for the MgOH isotopomer, and  $\alpha_1 = 100.6$  and  $\alpha_3 = 46.6$  MHz for the MgOD isotopomer. For the MgOH/MgOD bending mode  $v_2$ , it was attempted to reproduce the nonlinear dependence of  $\Delta B_v$  on the quantum numbers  $v_2$  and  $l_2$  with the quadratic formula<sup>32</sup> used in the experimental studies.<sup>6,8,9</sup> In those analyses, the quadratic formula was not found adequate to reproduce the experimental data. In this work, we also found it impossible. In the least-squares fit to the predicted changes  $\Delta B_v$ , the deviations between the predicted and fitted values were calculated to be as large as 18 MHz. The quality of the fit could also not be significantly improved by adding higher-order terms.

The slice through the *ab initio* potential energy surface of magnesium monohydroxide  $V(q_1, q_2, q_3)$  along the MgOH bending coordinate  $q_3$  is determined to be (see Table III)

$$V(q_1=0, q_2=0, q_3) = 80q_3^2 + 614q_3^4 - 77q_3^6 + 17q_3^8, \quad (2)$$

where the energy and  $q_3$  coordinate are given in wave numbers and radians, respectively, with the higher-order coefficients being smaller than  $1 \text{ cm}^{-1}$ . This is essentially a quartic function with the minimum at the linear MgOH configuration ( $q_3=0$ ). In comparison, the quadratic and quartic terms of the MgOH bending potential energy function were determined by Bunker *et al.*<sup>7</sup> to be 153 and  $523 \text{ cm}^{-1}$ , respectively. For the main MgOH isotopic species, the ground bending state is calculated to lie  $166 \text{ cm}^{-1}$  above the minimum of the function of Eq. (2), with the classical turning point located at the valence angle MgOH of  $141^\circ$ . The vibrational amplitude of the  $v_2$  mode in any of its energy levels

amounts thus to more than  $39^\circ$ . The predicted MgOH bending potential energy function and location of the low-lying bending energy levels are shown in Fig. 1. It is worth noting the qualitative change in relative location of the  $l_2$  sublevels on going from the  $v_2=2$  to  $v_2=4$  bending energy level. Concerning the quasilinear nature of the MgOH bending potential energy function, magnesium monohydroxide most closely resembles two other well-studied quasilinear molecules, namely fulminic acid (HCNO) (Refs. 33, 34) and cyanofulminate (NCCNO).<sup>35,36</sup> All of these three molecules were determined to be linear at equilibrium, with the bending potential energy function being extraordinarily flat near the minimum.

As shown in this work, using the state-of-the-art *ab initio* methodology, it was not necessary to resort to any empirical adjustments of the potential energy surface of magnesium monohydroxide to obtain results as good as in the previous theoretical study.<sup>7</sup>

## ACKNOWLEDGMENTS

J.K. would like to thank B. P. Winnewisser and M. Winnewisser for their helpful comments. G.T. and J.K. were supported in part by NATO Grant No. PST.CLG.978504 and Greek–Polish Project No. 3357/R00/R02. K.A.P. was supported by the Division of Chemical Sciences in the Office of Basic Energy Sciences of the U.S. Department of Energy.

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