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Ab initio calculations on the ground and excited states of BeOH and MgOH

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Ab initio configuration interaction calculations have been carried out on the ground and excited electronic states of the BeOH and MgOH molecules as well as of the cations $BeOH^+$ and $MgOH^+$, for linear and bent geometries. The excited states of the above molecules have not previously been calculated and experimental information exists only for the $A-X$ system in MgOH and MgOD. The present results show that in the excited states the molecules MgOH and BeOH have similar M–O (M=Mg,Be) stretching and bending potentials. In general, the stretching potentials are rather complicated, showing a number of avoided crossings. Furthermore, most of the excited states show minima at R near $R_{\min}$ of the corresponding cations $BeOH^+$ and $MgOH^+$, indicating Rydberg contributions to the molecular excited states. The first excited state in both BeOH and MgOH is $2\,^2A'$, which along with $1\,^2A''$, forms the $1\,^2\Pi$ state of linear geometries and which in both systems has minimum energy at a bent geometry with bond angle near 115°. In MgOH, the $2\,^2A'$ state is the A state of the observed $A-X$ spectra and the theoretical transition energy and the barrier to linearity are in good agreement with the corresponding experimental quantities. Analogous spectra for BeOH, not reported as yet, would be expected on the basis of the present calculations at higher energies than the MgOH spectra by 0.6 eV. The results on the molecular ground-state potentials are similar to those of previous calculations, showing a linear minimum geometry for MgOH but with a very shallow bending potential, and for BeOH a bent minimum but with only a 50 cm^{-1} barrier to linearity. © *1999 American Institute of Physics.* [S0021-9606(99)30846-1]

I. INTRODUCTION

The alkaline earth monohydroxides are the simplest monovalent polyatomic derivatives of the alkaline earths and have been observed in flames of alkaline earth salts since 1823 (Ref. 1 and references therein). These systems are the most studied of polyatomic alkaline earth-containing molecules and there exists considerable literature on their spectroscopy, mainly involving the heavier members of the alkaline earths. Of the two lighter, Be and Mg, only the $A-X$ system in MgOH (and MgOD) has been observed and analyzed in a laser excitation study.[2]

The electronic structure of monovalent alkaline earth radicals MX is conceptually simple involving a single electron outside a closed shell ‘‘core.’’[1,3] This model is particularly appropriate for the larger systems where the closed-shell core can by represented as an ionic pair M^+X^- and consequently the molecular geometries are linear in the ground as well as in excited electronic states, as is the case for example in CaOH and SrOH.[3] However, for MgOH and especially for BeOH, there seems to be significant covalent contribution and consequently the geometries deviate from linearity.

All previous calculations on MgOH and BeOH have been devoted to the ground electronic state. For MgOH the potential energy function and rovibrational levels have been determined recently[4] and the recent study as well as previous calculations[2,3] show that the ground state of MgOH is linear but with a very flat bending potential. The analysis of the high-resolution gas-phase laser excitation spectra of MgOH showed that the A state is bent with a barrier of about 1970 cm^{-1}, and is considered to be the lower Renner–Teller component originating from a $^2\Pi$ state.[2] For BeOH there is no laser spectroscopic information and even for the ground state the geometry has not been determined. A bent structure has been suggested for the ground state of BeOH, by extrapolation since Be has larger ionization potential than Mg[2] and theoretical work exists in agreement with that assumption.[3,5] However, the most recent *ab initio* work on this system[6] claims a quasilinear structure (with a bond angle of 179.5°), in agreement with one of the possible interpretations of earlier electron spin resonance (ESR) work.[7] In any case, the potential energy surface of the ground state of BeOH is very flat with respect to the bending mode. Indeed, the quasilinear minimum in the most recent theoretical study is lower in energy than the best bent structure by only 44 cm^{-1}, whereas in the previous studies the bent minimum is lower than the linear structure by 60 cm^{-1}[3] and 45 cm^{-1}.[5]

In the present work, *ab initio* multireference double excitations configuration interaction (MRD-CI) calculations[8,9] have been carried out on electronic states of MgOH and BeOH in an effort to provide information on the electronic structure of these systems, and in particular information on the potential energy surfaces of the excited electronic states, for which there have been no previous calculations, relevant to their spectroscopic observation.

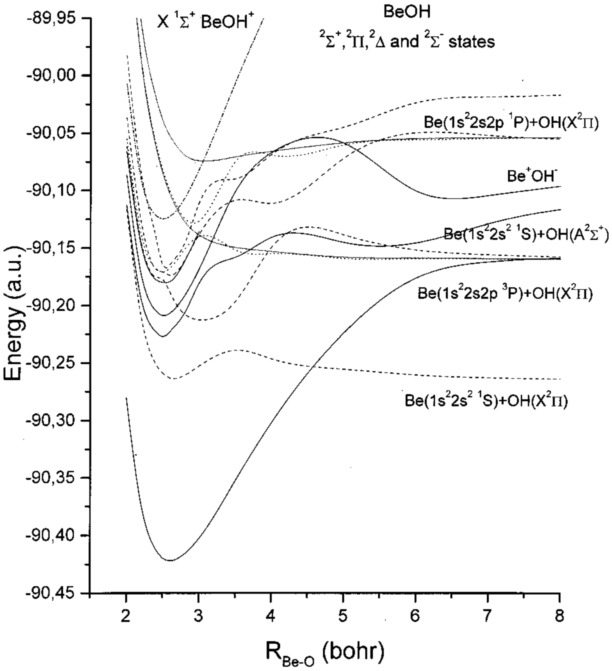

FIG. 1. Potential energy curves of electronic states of linear BeOH and the ground state of BeOH$^+$ with respect to stretching of the Be–O bond. Solid $^2\Sigma^+$ states, dash $^2\Pi$ states, short-dash $^2\Delta$, and dot $^2\Sigma^-$ states.

TABLE I. Vertical transition energies at the ground-state linear minimum energy geometry of BeOH and MgOH.

State	ΔE (eV) BeOH	ΔE (eV) MgOH
$X\ ^2\Sigma^+$	0.0[a]	0.0[b]
$1\ ^2\Pi$	4.32	3.62($2\ ^2A'$), 3.62($1\ ^2A''$)
	3.92[c] ($X\ ^2A'-2\ ^2A'$)	3.34($2\ ^2A'$)[c]
$2\ ^2\Sigma^+$	5.43	4.64($3\ ^2A'$)
$3\ ^2\Sigma^+$	5.86	⋯
$2\ ^2\Pi$	6.33	4.23($2\ ^2A''$)
$4\ ^2\Sigma^+$	6.61	⋯
$3\ ^2\Pi$	6.76	5.81($3\ ^2A''$)
$1\ ^2\Delta$	6.94($5\ ^2A_1$), 6.93($1\ ^2A_2$)	⋯
$4\ ^2\Pi$	7.02	⋯
$1\ ^2\Sigma^-$	8.64	⋯
$2\ ^2\Delta$	8.71	⋯
$1\ ^2\Sigma^-$	10.03	⋯
$X\ ^1\Sigma^+$	8.17	7.35
(MOH$^+$)	8.10[c]	7.23[c]

[a] Energy at linear minimum of BeOH—90.421 868 hartree.
[b] Energy at linear minimum of MgOH—275.341 036 hartree.
[c] $\Delta E_{\text{min-min}}$.

II. CALCULATIONS

Ab initio MRD-CI calculations have been carried out on electronic states of BeOH and MgOH for linear and bent geometries involving different values of the M–O bond length, varying from 1.8 to 10.0 bohr for BeOH and from 2.6 to 10.0 bohr for MgOH and values of the bond angle between 90° and 180°. The O–H bond length was fixed for most of the calculations on BeOH at 0.9435 Å, which was found to be the optimum value for linear BeOH[6] and for MgOH at 0.95 Å (as in Refs. 3 and 4).

A. Details of the calculations on BeOH

The atomic orbital (AO) basis sets employed consist of contracted Gaussian-type functions, $[10s\,6p/5s\,3p]^{10}$ plus two sets of *d* polarization functions (exponents 1.50, 0.35) and *s*, *p*, and *d* diffuse functions (exponents 0.032, 0.028, and 0.015, respectively[11]) for oxygen, $10s/5s(10)$, $5p/3p$ (as in Ref. 12) plus two sets of *d* polarization functions (exponents 0.96 and 0.32) for beryllium, and the $5s/3s$ basis set for hydrogen[11] augmented with two *s* functions (exponents 0.082 217 and 0.025) and three *p* polarization functions (exponents 0.7, 0.2, and 0.035).

The point group symmetry of the molecule in bent conformations is C_S and in this symmetry most of the calculations have been carried out. In order to identify the linear states, one additional set of calculations on linear conformations employed C_{2V} symmetry. In the C_{2V} calculations the $^2\Sigma^+$ states are obtained as $^2A_1$, the $^2\Pi$ states are obtained as $^2B_1$ and $^2B_2$, the $^2\Delta$ states as the $^2A_1$ and $^2A_2$, and the $^2\Sigma^-$ as $^2A_2$. Five roots of each of the $^2A_1$, $^2B_1$, and $^2A_2$ states were calculated using 85, 87, and 73 reference configurations, respectively, with respect to which all configurations resulting from single and double substitutions are generated and selection of configurations was carried out with a threshold of 1 microhartree in each case, which resulted in CI spaces of 40 000 to 80 000 configuration functions for the different geometries.

For the C_S calculations three states of $^2A'$ and two states of $^2A''$ symmetry were calculated at a total of 130 different geometries involving variations in the bond angle <BeOH and in the Be–O distance. The reference space consisted of 63 configurations for the $^2A'$ calculations and 78 configurations for the $^2A''$ and the selection threshold was again 1 microhartree. This resulted in around 70 000 selected configuration functions. Finally, linear stretching and bending potential energy curves have been calculated for the cation BeOH$^+$, which provide a guide for the interpretation of the Rydberg contribution to the potential energy curves of BeOH. For these calculations, seven reference configurations and selection threshold of 0.1 microhartree were employed. All the above sets of reference configurations have been determined on the basis of test calculations at different geometries in order to ensure as uniform a description as possible over the potential energy surfaces.

B. Details of the calculations on MgOH

The AO basis sets for the O and H atoms are as above for the calculations on BeOH but without the diffuse functions on O. For Mg the $[12s\,9p/6s\,4p]$ basis[13] was augmented with two *d* polarization functions (exponents 1.0 and 0.5) and *s*, *p*, and *d* diffuse functions (exponents 0.012, 0.010, and 0.015, respectively).

All the calculations on MgOH have been carried out in the C_S point group symmetry, and three roots of each sym-

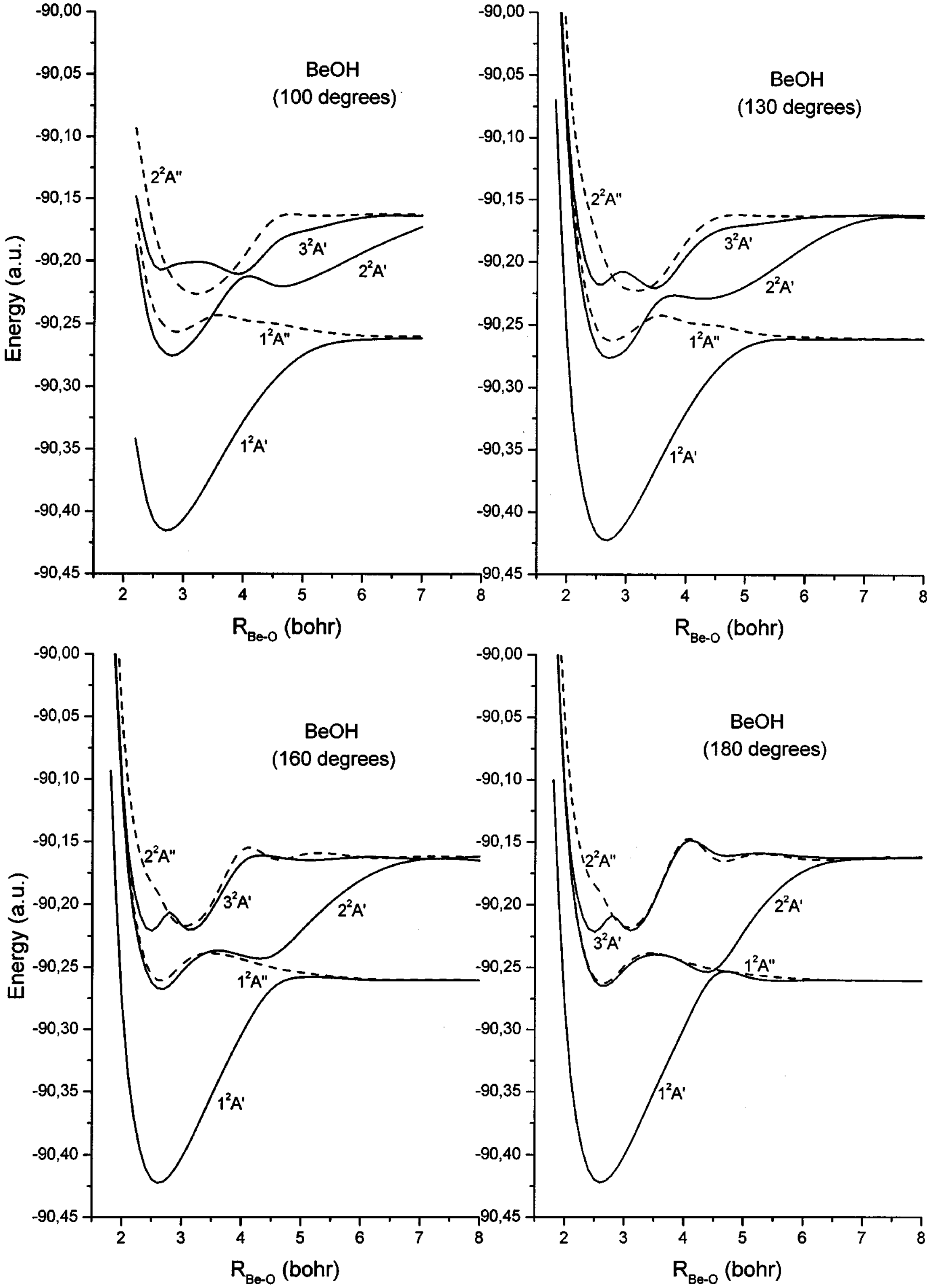

FIG. 2. Be–O stretching potential energy curves of the electronic states of BeOH at different values of the Be–O–H bond angle.

metry, $^2A'$ and $^2A''$, have been calculated. The reference spaces consisted of 75 and 71 configurations for the $^2A'$ and the $^2A''$ states, respectively, the selection threshold was 1 microhartree, and the resulting CI spaces varied between 30 000 and 77 000 configuration functions. At all the molecular geometries considered, the ground state of the cation $MgOH^+$ has also been calculated, using 35 reference configurations and selection threshold of 0.1 microhartree.

III. RESULTS AND DISCUSSION

A. Calculations on BeOH

The C_{2V} calculations yielded four $^2\Sigma^+$, two $^2\Delta$, two $^2\Sigma^-$, and five $^2\Pi$ electronic states of BeOH. Their potential energy curves as a function of the Be–O bond length, for fixed O–H bond length at 0.9435 Å,[6] are plotted in Fig. 1, along with the stretching potential of linear $BeOH^+$. As

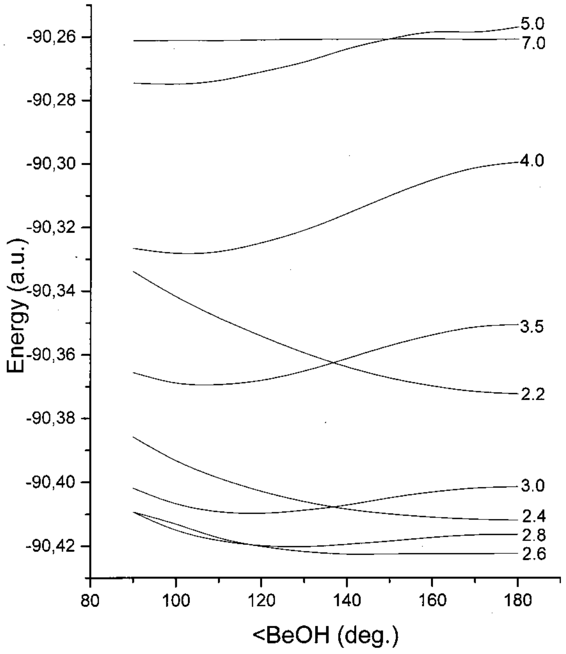

FIG. 3. Bending potentials of the ground state of BeOH at different values of the Be–O bond length, as indicated (in bohr).

shown in Fig. 1, the $X\,^2\Sigma^+$ potential energy curve correlates (along with $2\,^2\Pi$, $1\,^2\Delta$, and $1\,^2\Sigma^-$) with excited Be dissociation limits Be $(1s\,^22s2p\,^3P^0)+\mathrm{OH}(X\,^2\Pi)$, while the first $^2\Pi$ state is the lowest state at Be–O distances larger than 4.5 bohr and correlates with ground-state limits Be $(1s\,^22s^2\,^1S)+\mathrm{OH}(X\,^2\Pi)$. The next higher $^2\Sigma^+$ state correlates with $\mathrm{Be}(1s\,^22s^2\,^1S)+\mathrm{OH}(A\,^2\Sigma^+)$ limits, while the third $^2\Sigma^+$ state at bond length larger than 4.5 bohr has ionic character, $\mathrm{Be}^+\mathrm{OH}^-$. The next higher dissociation limit, Be $(1s\,^22s2p\,^1P^0)+\mathrm{OH}(X\,^2\Pi)$, collects at large R the potential energy curves of the $3\,^2\Pi$, $2\,^2\Delta$, and $2\,^2\Sigma^-$ states since the fourth $^2\Sigma^+$ state was only obtained for a Be–O bond length shorter than 3.5 bohr.

The stretching potential energy curve of the $X\,^2\Sigma^+$ state (Fig. 1) shows a deep minimum at $R_{\mathrm{Be-O}}$ of 1.3775 Å of 7.09 eV, which, however, cannot be associated with the dissociation energy of the Be–OH bond, since in C_S symmetry the curve crossing at 4.5 bohr becomes avoided and a lower dissociation energy is obtained. As shown in Fig. 1, the potential energy curves of the excited states are complicated as a result of avoided crossings, caused by interactions between different types of states such as valence–Rydberg (at short $R_{\mathrm{Be-O}}$) and covalent–ionic (between the $^2\Sigma^+$ states at large R). The stretching potential of the cation is very steep and with a minimum at 2.5 bohr, at which bond length Rydberg minima are also found in the excited states of BeOH (cf. Fig. 1). The vertical transition energies of the electronic states of BeOH, at the ground-state lowest energy linear structure are listed in Table I, along with corresponding quantities for MgOH, which shall be discussed below.

The calculations in C_S symmetry involved different geometries (including linear structures) resulting from variations in the Be–O bond length and the <BeOH angle with the O–H bond length fixed at the optimum value for the ground-state linear geometry of previous work,[6] 0.9435 Å. Some variation in the O–H bond length was also considered, once the optimum bent structure for the ground state was determined. For the C_S calculations, we consider the lowest three A' and the lowest two A'' states. The calculated energies at the 130 different geometries may be obtained directly from the authors. In what follows, features of the potential energy surfaces shall be discussed with the aid of plots.

In Fig. 2, the stretching potentials of the different states at bond angles of 100, 130, 160, and 180° are plotted. It may be seen that there are small variations in the stretching potentials with bond angle, with the states becoming more and more separated at smaller bond angles. In Fig. 3, the bending potential of the ground electronic state of BeOH at different values of $R_{\mathrm{Be-O}}$ are given. As shown, at $R_{\mathrm{Be-O}}\leqslant 2.4$ bohr the bending potentials are monotonic and have a minimum at the linear geometry. For larger values of $R_{\mathrm{Be-O}}$, a barrier to linearity is obtained, slight at $R_{\mathrm{Be-O}}=2.6$ bohr (cf. Fig. 3), and increasing with increasing $R_{\mathrm{Be-O}}$ with the maximum barrier reached at $R_{\mathrm{Be-O}}=4.0$ bohr and decreasing again after that. The bending potentials of all the electronic states, at the optimum $R_{\mathrm{Be-O}}$ value in each case, are plotted in Fig. 4, where the vertical scale is different for the different plots. The lowest energy molecular geometry of the ground state is at $R_{\mathrm{Be-O}}=2.6$ bohr and bond angle of 142.5°, at energy only 50 cm^{-1} below the linear minimum. The first excited state, $2\,^1A'$, is bent with a minimum at a bond angle of 116° at $R_{\mathrm{Be-O}}=2.8$ bohr and has a barrier of 3710 cm^{-1} to linearly. This value is an overestimate (as are the values for all the barriers mentioned below) since geometry optimization might lower it. The $1\,^2A''$ state, which along with $2\,^2A'$ correlates with $1\,^2\Pi$ of the linear geometries, at 2.8 bohr favors a bent structure (bond angle 130°), with a very low barrier to linearity at 160° of 940 cm^{-1}, while at 2.6 bohr the barrier almost disappears. Similarly, $3\,^2A'$ with $R_{\mathrm{Be-O}}$ of 2.4 bohr favors a linear structure, while $2\,^2A''$ with $R_{\mathrm{Be-O}}$ at 3.0 bohr favors a bent structure with bond angle of 115° and shows a barrier to linearity of 1676 cm^{-1} at 170°.

Two bending potentials have been generated for the cation, BeOH^+. One is at Be–O and O–H bond lengths similar to those of the linear minimum of BeOH and one at the optimum values for the cation, Be-O of 2.5 bohr and O–H of 1.8047 bohr (or 0.955 Å), determined in the present work. Both potentials have a minimum at 180°.

B. Results of the calculations on MgOH

Calculations have been carried out on MgOH and on MgOH^+, in C_S symmetry, at 170 different geometries and the calculated energies may be obtained directly from the authors. The stretching potentials of the electronic states calculated in the present work for bond angles of 90, 120, 150, and 180° have been plotted in Fig. 5. As shown, the stretching potentials of the excited states of MgOH are complicated by avoided crossings and generally are similar to those of the excited states of BeOH.

The bending potentials of the ground state $(X\,^2A')$ and the $2\,^2A'$ and $1\,^2A''$ states, at Mg–O bond length of 3.4 bohr are plotted in Fig. 6. As expected, the ground state of MgOH has a very shallow bending potential with the minimum at

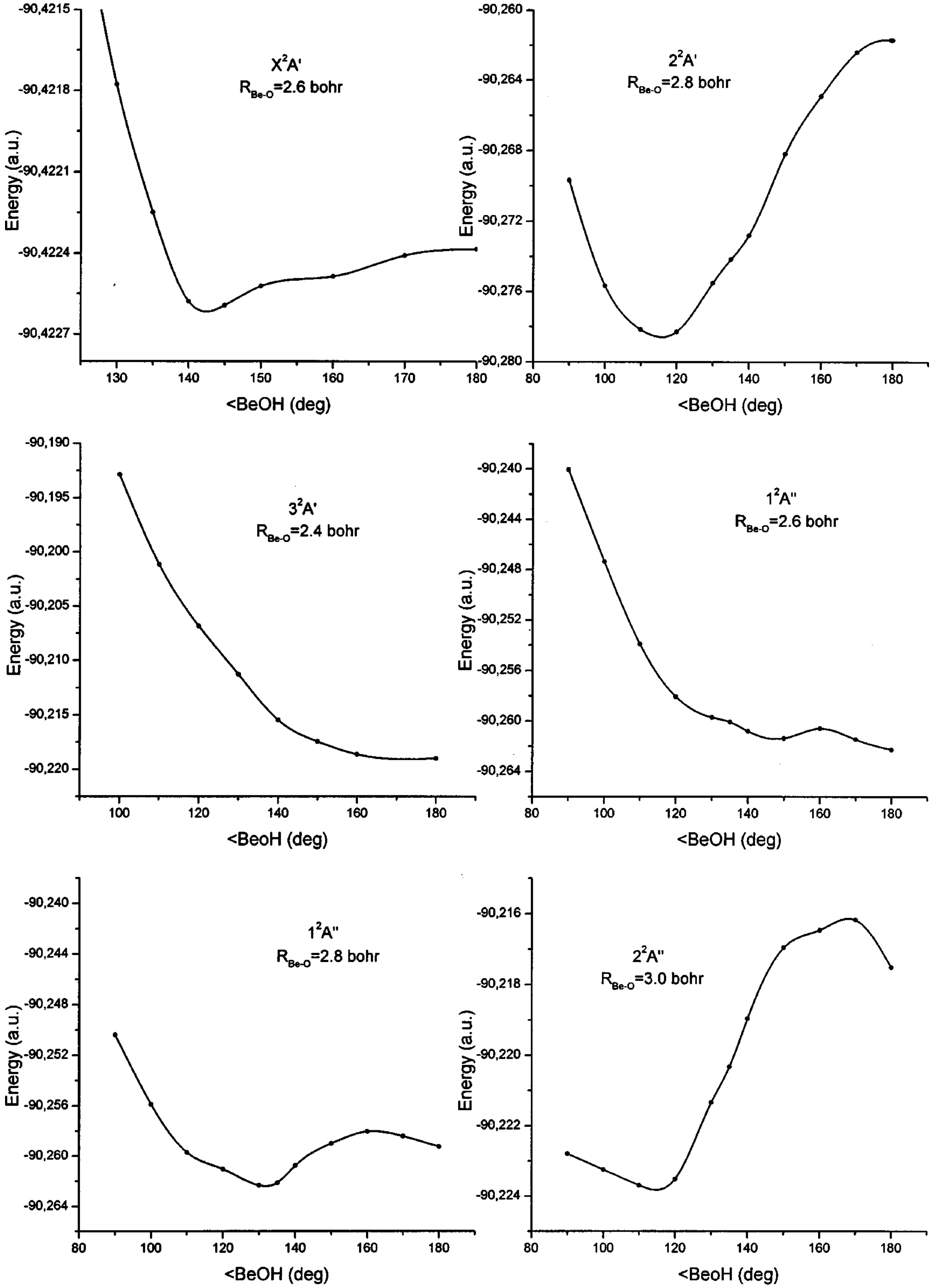

FIG. 4. Bending potentials of electronic states of BeOH, at the optimum $R_{\mathrm{Be-O}}$ for each state.

the linear geometry. The present calculations find a slight barrier at 170° of about 26 cm^{-1}, whereas in the experimental work a barrier of under 2 cm^{-1} is estimated.[2] Again, geometry optimization might lower the 26 cm^{-1} value, but such small energy differences are well within the error limits of the *ab initio* calculations. As mentioned in the Introduction, the ground state of MgOH has been previously treated in detail, including calculation of the potential energy function and rovibrational levels.[4] Thus, it shall not be dealt with any further in the present work.

The first two excited states of MgOH, $2\,^2A'$ and $1\,^2A''$, which at linear geometries are degenerate and form the $1\,^2\Pi$ state, at $R_{\mathrm{Mg-O}}$ of 3.4 bohr favor bent geometries (see Fig. 6). The minimum of the first excited state, $2\,^2A'$, which is the A state in the observed $A-X$ spectra of MgOH[2] is found at a bond angle of 115° with a difference in the electronic energy

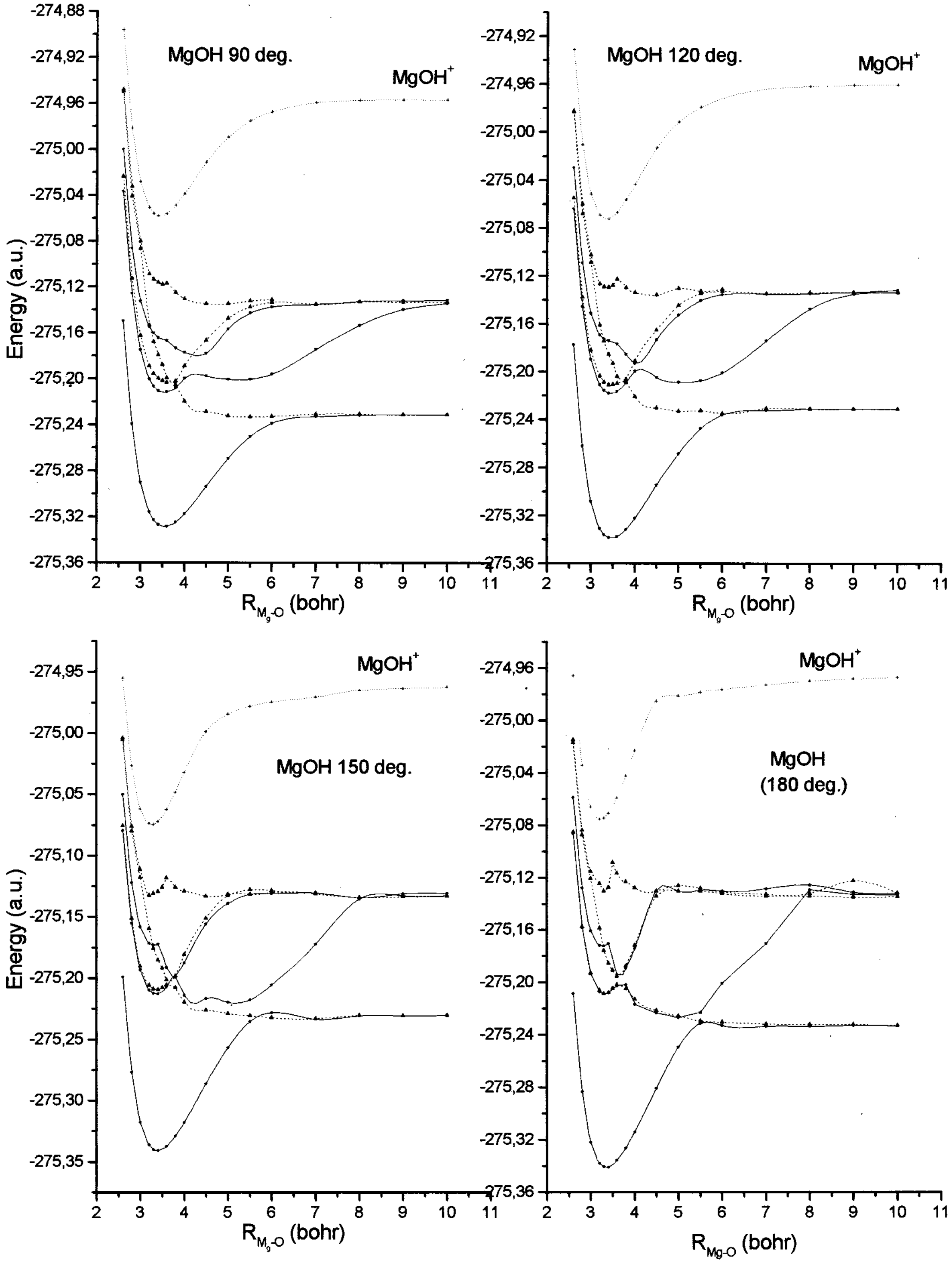

FIG. 5. Mg–O stretching potentials of electronic states of MgOH at different values of the bond angle as indicated.

between the bent and the linear structure of 2216 cm^{-1}. The experimental value for the bond angle is 119°, for the Mg–O bond length is 3.394 bohr, and for the barrier height is 1970 cm^{-1}. Thus, the agreement between the theoretical and the experimental quantities regarding the Mg–O bond length and the barrier height is very good, while there is a difference of 4° between the theoretical and the experimental value for the bond angle.

The transition energies of the excited states of MgOH with respect to the ground-state minimum are listed in the third column of Table I, where the vertical (at the ground-state minimum energy geometry) and adiabatic ($\Delta E_{\mathrm{min-min}}$) electronic energy differences in eV are listed. The calculated adiabatic $A-X$ transition energy, 3.34 eV, is within 0.05 eV of the observed value (26 606 cm^{-1} or 3.299 eV for the $00\,{}^{1}0-00\,{}^{0}0$ transition[2]) and thus the present calculations support the experimental assignment that the A state is the lower Renner–Teller component of the $1\,{}^{2}\Pi$ state of MgOH.

The bending potentials of the ground state of the cation, MgOH^{+}, at different Mg–O bond lengths are plotted in Fig.

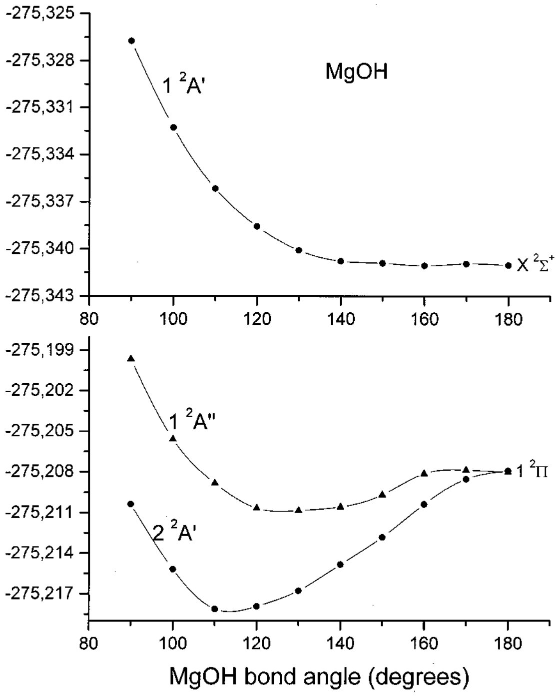

FIG. 6. Bending potentials of the ground state (upper plot) and the 2 $^2A'$ and 1 $^2A''$ states of MgOH at $R_{\mathrm{Mg-O}}$ of 3.4 bohr.

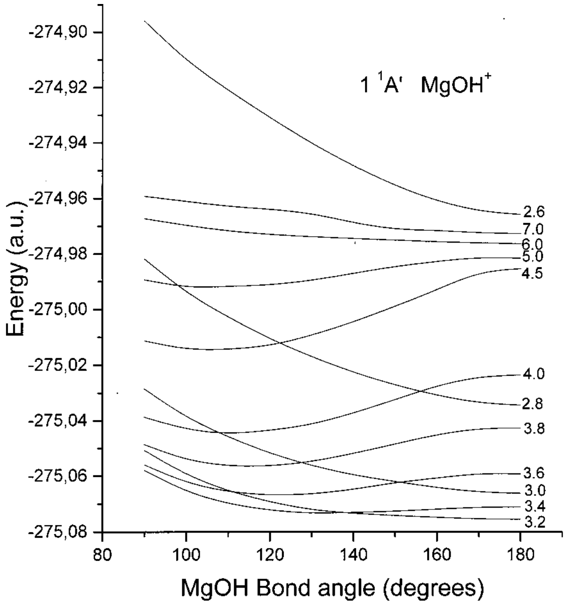

FIG. 7. Bending potentials of the ground state of MgOH$^+$ at different values of $R_{\mathrm{Mg-O}}$ as indicated (in bohr).

7. As shown in Fig. 7, the same type of pattern found in the bending potentials of BeOH (cf. Fig. 3) is shown here as well, i.e., at short bond lengths the minimum is at the linear geometry while at large bond lengths bent minima are found. The lowest energy structure is linear with a Mg–O bond length of 3.2 bohr, with energy lower than the bent structure at Mg–O of 3.4 bohr by 512 cm^{-1}. Thus, the ground-state potential of the cation shows the same type of shallow bending potential as found in the ground states of these molecules.

IV. CONCLUSION

Ab initio MRD-CI calculations on the ground- and excited electronic states of MgOH and BeOH and on the cations BeOH$^+$ and MgOH$^+$ have been presented. The results on the ground-state potential energy surfaces of MgOH and BeOH are in agreement with previous work, indicating very shallow bending potentials. The main object of the present work has been the calculation of the excited states of BeOH and MgOH, for which the present are the first such calculations. In the present work, M–O stretching potentials at different bond angles and bending potentials at different M–O bond lengths have been generated for M=Mg,Be. The results of the calculations on the 2 $^2A'$ state of MgOH are in good agreement with experimental data derived from analysis of the $A-X$ spectra of this system. Analogous spectra for BeOH are predicted at higher energies than the spectra of MgOH by about 0.6 eV.

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