

***Ab initio* study of the electronic spectrum of BeO**

IVANA ADAMOVIĆ,* MAJA PARAC,* MICHAEL HANRATH** and MILJENKO PERIĆ*

*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 16, YU-11000 Belgrade, Yugoslavia and **Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

(Received 11 June 1999)

Low-lying singlet and triplet electronic states of the BeO molecule are calculated by means of the quantum chemical *ab initio* method. It was found that all states in the energy range from 0 to 50000 cm⁻¹ are of valence character. Particular attention was paid to the investigation of the dissociative behavior of the states considered. The vibrational structure of the A¹P < X¹S and B¹S⁺ < X¹S⁺ spectral systems was calculated.

Keywords: electronic spectrum, *ab initio* calculations, valence - Rydberg interaction

The spectrum of the first member of the alkaline earth oxide family, BeO, has been less studied than those of its heavier homologues (MgO, CaO,...). This concerns particularly experimental investigations which have been restricted to a relatively small number of spectral systems. A great deal of experimental information stems from a series of papers published by Lagerqvist about fifty years ago.¹⁻⁷ On the basis of these data, four electronic states of the same multiplicity, X, A, B and C have been identified and the corresponding spectroscopic constants determined.⁸ In a combined experimental and theoretical *ab initio* study Lavende *et al.*⁹ improved these parameters and also obtained data for the a³P state. Isotopic shift studies of the B-X system of BeO were carried out by Bojović *et al.*¹⁰ and Antić-Jovanović *et al.*¹¹ Other experimental methods (mass spectrometry, thermodynamics)¹²⁻¹⁴ have been employed to obtain additional information on some structural parameters (*e.g.* the dissociation energy). Recently, the spectra of a number of molecular species involving beryllium and oxygen atoms have been recorded.¹⁵⁻¹⁷

Beryllium oxide is a species of considerable interest to theoreticians. It is an ionic molecule, but its electronic states are characterized by electron occupations corresponding to different formal charges on the atoms, Me^{+d}O^{-d}, 0 < d < 2. Due to the existence of several close lying low-energy dissociation channels, it is expected that BeO has many low-lying electronic states. Early *ab initio* studies, not consid-

ering the electron correlation effects,^{18–21} were not successful in obtaining reliable results concerning the energetics of the low-lying electronic states. So, for example, at the Hartree-Fock (HF) level of sophistication, the 1^1P state was found to lie below the lowest-energy 1^1S^+ species,²⁰ expected to represent the ground electronic state. The correct ordering of the low-lying electronic states of BeO (X^1S^+ , 1^3P , 1^3S^+) was first achieved in *ab initio* studies including the electron correlation, carried out by Schaefer *et al.*^{22–24} A series of highly sophisticated theoretical studies by Bauschlicher *et al.*^{25–28} has led to the accurate determination of structural parameters, particularly of the dissociation energy, in the ground and several excited states of BeO. The complete potential energy curves, up to the dissociation limit have been published in a few papers.^{29–30} A number of papers report calculations of various molecular properties in the ground state of the molecule.^{31–40} Finally, because of the small number of electrons and its special features, BeO has been used as a molecule for testing various new theoretical approaches.^{34,39,41–47}

Except for the work by Irisawa and Iwata,³⁰ all the theoretical studies published so far concern a very limited number of low-lying electronic states of BeO. Particularly, information about the states of Rydberg character and of their relationship to the valence-type species is completely missing. The goal of the present study was to fill this gap. The investigations were extended to all singlet and triplet electronic states lying in the energy range between 0 and roughly 60000 cm⁻¹, involving also the lowest members of the Rydberg series.

TECHNICAL DETAILS

The calculations presented in this paper were carried out by means of the combined self-consistent field (SCF) and the multi reference single and double excitation configuration interaction (MRD-CI) method.⁴⁸ Two atomic orbital (AO) basis sets were employed. The first one (it shall be called basis A) involves only valence-type atomic orbitals (AOs). Both the beryllium and oxygen atoms are described by the (10s,4p,3d) Gaussian sets in the [4s, 2p, 1d] contraction, proposed by Pierloot *et al.*⁴⁹ In order to enable a description of lowest members of the Rydberg series, a set of calculation was carried out with the above valence basis augmented by 3s, 3p, 3d and 4s Cartesian Rydberg AOs (exponents $a_{3s} = 0.019$, $a_{3p} = 0.015$, $a_{3d} = 0.015$, and $a_{4s} = 0.0047$). This AO set will be called basis B. The basis sets of such a modest size are not expected to ensure high numerical accuracy of the results, but should enable a reliable description of the global structure of the electronic spectrum of BeO.

All calculations were carried out technically in the framework of the C_{2v} subgroup of the $C_{\infty v}$ molecular point group. The molecular orbitals (MOs), employed as the one-electron basis in the configuration interaction calculations, were generated in the complete active self consistent field (CASCf)⁵⁰ calculations involving 10 electrons (1s electrons of Be and O were kept frozen) variably distributed between 6 active orbitals, $1p$ ($1b_1 + 1b_2$ in terms of the C_{2v} irreducible

representations), $4s(4a_1)$, $5s(5a_1)$ and $2p(2b_1+2b_2)$. The CI calculations were carried out with the DIESEL-CI program package.⁵¹ The CI treatment was of the standard MRD-CI type with configuration selection and energy extrapolation.⁴⁸ The effect of higher than double excitations with respect to the most important (reference) configurations was estimated by means of a Davidson-type perturbative formula.⁵²

The electronic energies for five (in the case of AO basis A) or eight (AO basis B) lowest-lying singlet and triplet states belonging to each of the irreducible representations of the C_{2v} point group were calculated as the Be–O separation varied between 1.8 bohr (1 bohr = 0.52917 Å) and 4 bohr (basis B) with an increment of 0.2 bohr; additional calculations are carried out at Be–O distances of 4.5, 5.0, 5.5, 6.0, 7.0 and 10.0 bohr. The number of reference configurations employed in the calculations varied between 10 and 100, and the number of configurations selected according to the energy lowering criterion $T = 5$ mhartree (basis A, 1 hartree = 27.21 eV) and $T = 2$ mhartree (basis B) between 10000 and 100000, depending on the electronic state symmetry and molecular geometry.

RESULTS AND DISCUSSION

Potential energy curves for low-lying singlet and triplet electronic states of BeO

A very useful tool for the understanding of the structure and features of molecular electronic spectra is the analysis of the composition and energy of the MOs employed as the one-electron basis in the CI calculations, particularly of their change with geometry variations. The energies of the low-lying MOs, obtained in the HF calculations employing the AO basis not including Rydberg-type orbitals, as function of the Be–O bond length are displayed in Fig 1. The two MOs with the lowest energy (not shown in Fig. 1), $1s$ and $2s$, are formed by the $1s$ AOs of the oxygen and beryllium atoms, respectively. The electrons populating these orbitals do not contribute significantly to the binding of the atoms in the molecule. The next three orbitals in order of increasing energy are $3s$, $1p$ and $4s$, all of them (as well as the $1s$ and $2s$) are doubly occupied in the ground electronic state of BeO. At all values of Be–O separation, the $3s$ orbital is composed predominantly of the $2s$ of AO of oxygen and the $1p$ MO by the $2p_x, 2p_y$ pair of the oxygen AOs. The $4s$ orbital consists, at smaller Be–O bond lengths and particularly at the equilibrium Be–O value, of the $2p_z$ oxygen AO, admixed by the beryllium $2s$ orbital. At larger Be–O distances the contribution of the latter species increases continuously so that the $2s$ Be orbital becomes dominant at the dissociation limit. The energy of all of these three MOs increases with elongation of the Be–O distance, indicating their binding character. The two lowest-lying MOs not occupied in the ground state of BeO, the $5s$ and $2p$ possess similar energies (close to zero), relatively weakly depending on the molecular geometry. The composition of the $5s$ species is complementary to that of the $4s$: at small Be–O distances its main component is $2s$ Be admixed by the $2p_z$ oxygen AO; at large Be–O separation the situation is reversed. The $2p$ orbital

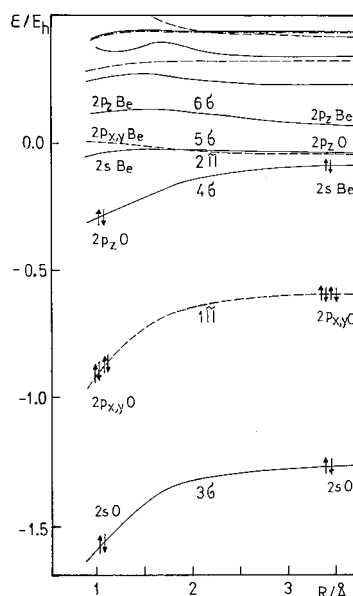


Fig. 1. Dependence of the MO energies of BeO, obtained in calculations employing AO basis A (without Rydberg functions), on the Be–O bond length. Solid lines: s species; dotted lines: p MOs; dash-dotted lines: dMOs. The AO character of the low-energy MOs is indicated.

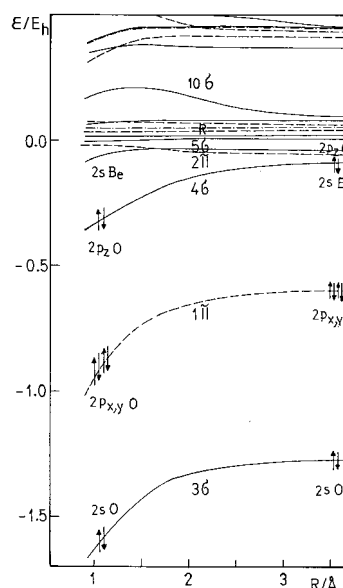


Fig. 2. Dependence of the MO energies on the Be–O distance, obtained in calculations using the AO basis B, involving Rydberg-type functions. For key to notation see Fig. 1.

consists of the $2p_x$ and $2p_y$ Be AOs. The next virtual orbital in increasing energy order ($6s$) lies at an energy of about 0.1 hartree.

At infinitely separated beryllium and oxygen atoms, the energy associated with the $1p$ and $5s$ orbitals, consisting of $2p$ oxygen AOs, should be the same; the same applies to the $2p$ ($2p_x$, $2p_y$, Be AOs) and the $6s$ ($2p_z$ Be) species. Such a degeneracy is not achieved in the present calculations, being an artifact of the restricted Hartree-Fock (RHF) approach employed. However, this does not influence the results of the calculations for the electronic states considered.

Figure 2 shows how the situation is changed when the AO basis also involves Rydberg functions. The geometry dependence of the orbital energies and the composition of the MO species, occupied in the ground electronic state, as well as of the lowest-energy virtual MOs, $5s$ and $2p$, is very similar to that presented in Fig. 1. On the other hand, the MO with the energy and composition corresponding roughly to the $6s$ species of Fig. 1 becomes $10s$ when the AO basis involves $3s$, $4s$, $3p$ and $3d$ Rydberg orbitals. This is a consequence of the fact that the lowest-lying virtual MOs, $6s$ – $9s$ (as well as $3p$, $4p$, $1d$), are now of predominantly Rydberg character. The character of these MOs is typical for Rydberg-type species: their energy is close to zero and shows almost negligible change with variations of the Be–O distance.

The ground electronic state of BeO corresponds to the distribution of its twelve electrons among the lowest-energy MOs available: $1s^2 2s^2 3s^2 1p^4 4s^2$. The symmetry of this state is thus $^1S^+$. The low-lying excited electronic states arise by one- or two-electron excitations out of the highest-energy MOs occupied in the ground state, $1p$ and $4s$, into the lowest-energy virtual MOs, $5s$, $2p$ and the Rydberg-type orbitals. The states resulting by one-electron excitations into the low-lying virtual valence orbitals are collected in Table I. The electronic states of BeO correlating with the five lowest-lying dissociation channels, involving combinations of the 1S and 3P states of beryllium and the 3P , 1D and 1S states of oxygen are given in Table II. The results of the calculation of the potential energy curves for low-lying singlet and triplet states of BeO are displayed in Figs. 3, 4 (AO basis not involving Rydberg functions) and 5, 6 (AO basis B with $3s$, $3p$, $3d$ and $4s$ Rydberg functions). The results of the calculation of the spectroscopic constants for the three most important species, X^1S^+ , A^1P and B^1S^+ , are given in Table III.

TABLE I. Leading electronic configurations of the low-lying electronic states of BeO

Exc.	Conf.	State
	$\dots 1p^4 4s^2$	$^1S^+$
$4s \rightarrow 5s$	$\dots 1p^4 4s 5s$	$^1S^+, ^3S^+$
$4s \rightarrow 2p$	$\dots 1p^4 4s 2p$	$^1P, ^3P$
$1p \rightarrow 5s$	$\dots 1p^3 4s^2 5s$	$^1P, ^3P$
$1p \rightarrow 2p$	$\dots 1p^3 4s^2 2p$	$^1S^+, ^1S^-, ^1D, ^3S^+, ^3S^-, ^3D$

TABLE II. Low-lying channels for the dissociation of BeO into Be and O atoms. Therm values given in the Table are taken from Ref. 53

Be	O	E/cm ⁻¹	BeO
1S_g	3P_g	0	$^1S + ^1P$
1S_g	1D_g	15868	$^1S^+ + ^1P + ^1D$
3P_u	3P_g	21978	$2^1S^+ + 1^1S^- + 2^1S^- + 2^1P + 3^1P + 2^1D +$ $1^3S^+ + 2^3S^- + 3^3S^- + 2^3P + 3^3P + 1^3D +$ $1^5S^+ + 1^5S^- + 2^5S^- + 1^5P + 2^5P + 1^5D$
1S_g	1S_g	33793	3^1S^+
3P_u	1D_g	37846	$4^1S^+ + 5^1S^+ + 3^1S^-$ $+ 4^1P + 5^1P + 6^1P + 3^1D + 4^1D + 1^1F +$ $2^3S^+ + 3^3S^+ + 4^3S^-$ $+ 4^3P + 5^3P + 6^3P + 2^3D + 3^3D + 1^3F$

A global characteristic of the low-energy electronic spectrum of BeO is the relatively minor role of Rydberg-type states (for comparison with other molecules the reader is referred to a recent book devoted to this subject⁵⁴). All electronic states computed to lie in the energy range between 0 and 50000 cm⁻¹, particularly those

investigated experimentally,⁸ possess exclusively, or at least predominantly, valence character. The first members of the Rydberg series appear at roughly 55000 cm^{-1} above the ground electronic state at its equilibrium geometry (compare Fig. 3 with 5 and 4 with 6). The leading configuration in the ground state, X^1S^+ , is $\dots 1p^4 4s^2$, but, as already noted in previous theoretical studies,^{24–28} the configuration mixing plays an important role for the proper description of this species. Present calculations overestimate the equilibrium bond length in the ground state by 0.044 Å ; the same applies to the other two states, A^1P , B^1S^+ , focused on in the present study, so that the relative values for the equilibrium Be–O distances in these states are in quantitative agreement with the corresponding experimental findings (see Table III). Such an uniform overestimation of the equilibrium bond lengths has also been obtained in previous *ab initio* studies carried out at similar levels of sophistication. The computed harmonic vibrational frequency is about 5% smaller than the experimentally determined value. On the other hand, the anharmonicity constant computed in the present study is in very good agreement with the corresponding experimental finding.

TABLE III. Comparison of the results of the present *ab initio* calculation of the spectroscopic constants in the X^1S^+ , A^1P and B^1S^+ states of BeO with those obtained in previous theoretical and experimental studies. a: Ref. 22; b: Ref. 26; c: Ref. 9; d: Ref. 28; e: Ref. 30; f: Ref. 28; exp: Ref. 8. The dissociation energy is given with respect to the lowest channel $\text{Be}(^1S)+\text{O}(^3P)$. ^g: D_0 value ($D_0 = D_e - 0.092\text{ eV}$). i: thermochemically derived value; ^j: result of extrapolation of vibrational progressions

State	Ref. $r/\text{\AA}$	T_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	D_e/eV	
X^1S^+	this work	1.375	0	1405	12	3.97
	a	1.313	0	1629	12.27	4.61
	b	1.377	0			
	c	1.342	0	1476	12.52	
	d					4.69g
	e	1.369	0	1472		4.3
	f	1.395				2.809
	exp.	1.3309	0	1487	11.830	4.6g,i 3.9,4.8g,j
A^1P	this work	1.503	7500	1090	8.5	
	b	1.508	8800			
	c	1.456	8300	1204	10.27	
	d	1.456		1167		
	e	1.479	7340	1130		
	f	1.547	5533			
	exp.	1.4631	9406	1144	8.415	
B^1S^+	this work	1.405	20400	1300	7.5	
	b	1.401	20517			
	c	1.362	18816	1468	9.04	
	e	1.355	19920			
	exp.	1.3623	21254	13671	7.746	

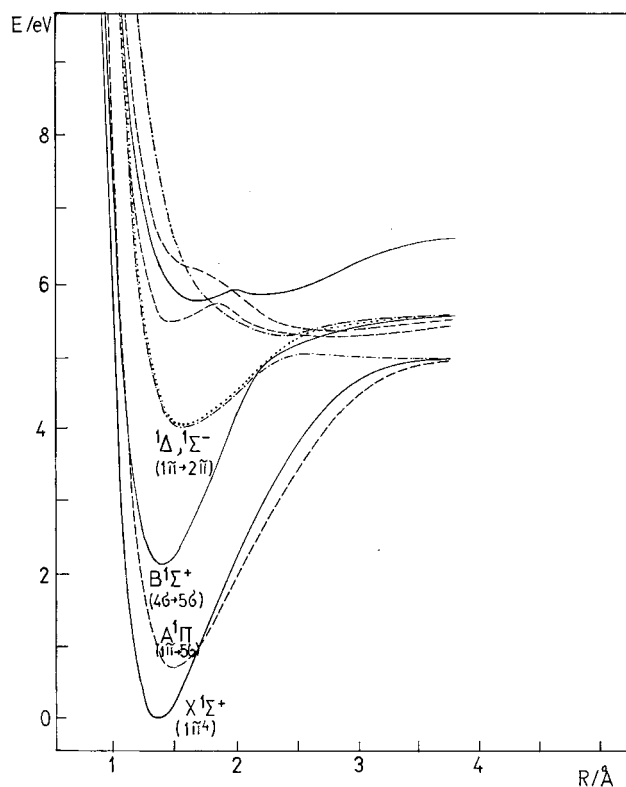


Fig. 3. Potential energy curves for the singlet states of BeO calculated employing AO basis A (without Rydberg orbitals). Solid lines: states of S^+ symmetry; dotted lines: S^- states; dashed lines: P states; dash-dotted lines: D states. The leading electronic configurations for the states considered are indicated. The zero on the energy scale corresponds to the minimum of the $X^1\Sigma^+$ state. An energy of 1 eV corresponds to 8066 cm^{-1} .

The estimation of the dissociation energy for BeO has been the subject of much controversy. The ground state of BeO does not correlate with the lowest-energy dissociation channel involving Be and O atoms in their respective ground states, 1S and 3P , but with the second channel in the increasing energy order, $\text{Be}(^1S)+\text{O}(^1D)$. Different values for the dissociation energy have been derived from experimental findings. On the basis of the extrapolation of the vibrational spacings in the $X^1\Sigma^+$ and $A^1\Pi$ states, Lagerqvist⁷ estimated values of D_0 of 3.9 and 4.8 eV for the dissociation of the ground electronic state of BeO into Be and O atoms in the ground atomic states. Another result ($D_0 = 4.6\text{ eV}$) stems from mass-spectrometry experiments.¹² Various theoretical approaches to obtain reliable dissociation energy have been discussed *e.g.*, in Ref. 30. The result of the present study, obtained as the difference between the directly computed values of the electronic energy of separated Be and O atoms and the ground state of BeO at its equilibrium bond length,

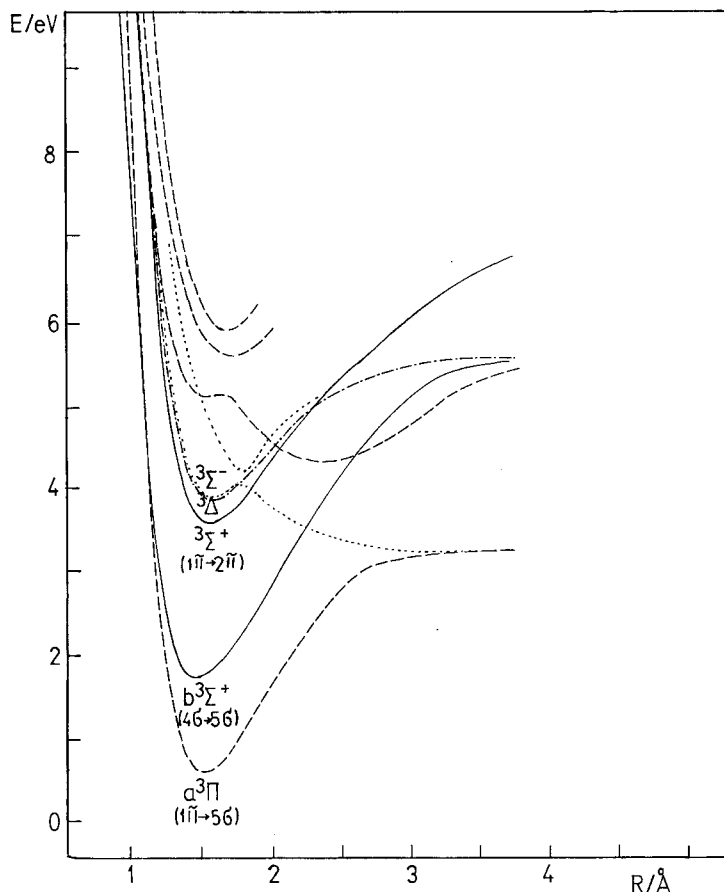


Fig. 4. Potential curves for the triplet states of BeO computed using AO basis A (without Rydberg functions). For key to notation see Fig. 3.

is $D_e = 3.97$ eV, corresponding to $D_0 = 3.88$ eV. The ground electronic state of BeO dissociates adiabatically into the channel involving the Be atom in its $1s^2 2s^2 {}^1S$ ground state and the O atom in the excited $1s^2 2s^2 2p^4, {}^1D$ state.

The lowest-lying singlet excited state of BeO is A^1P , with the dominant configuration arising by a $1pfi$ $5s$ one-electron excitation with respect to the ground state configuration. As a result of the partial depopulation of the strongly bonding $1p$ orbital in favor of the non-bonding $5s$ MO, the Be–O bond is weakened, resulting in an elongation of the equilibrium Be–O distance with respect to the value in the ground state. Comparison of the computed values for the spectroscopic constants with the corresponding experimental findings shows the same trends as in the ground state. The electronic transition energy obtained in the present study is roughly 0.2 eV below the experimentally derived T_e value. This relatively large discrepancy could be ascribed to the modest level of sophistication of the present theoretical

treatment, particularly to the deficiencies of the AO basis set employed: as already noted, the electron correlation plays a much smaller role in the A^1P state than in the other species considered, with the consequence that the energy of that state is calculated more satisfactorily (*i.e.*, relatively lower) than that of the ground and most of the other states considered. The A^1P state correlates with the same dissociation channel as the ground state.

The next singlet state in increasing energy order is B^1S^+ . Over a large range of the Be–O bond lengths, its main electronic configuration corresponds to a $4s\ 5s$ excitation. As a consequence of the bonding character of the $4s$ orbital, somewhat less pronounced than that of its $1p$ counterpart, the equilibrium bond length in this state is larger than in the ground state, but smaller than in the A^1P species. At large Be–O separations, the second adiabatic state of $^1S^+$ symmetry undergoes avoided crossings with other species of the same symmetry, changing in this way its electronic configurations. It arrives in the dissociation channel involving the $1s^2\ 2s\ 2p$, 3P state of Be and the $1s^2\ 2s^2\ 2p^4$, 3P state of O.

The next two singlet states, 1^1D and 1^1S^- lie very close to each other and correspond to $1p\ 5p$ one-electron excitations. The electronic transitions from the ground state to these species are dipole forbidden. Their equilibrium bond lengths are appreciably larger than in the ground state, because of the promotion of an electron from the strongly bonding $1p$ orbital into the non-bonding $2p$ species. The 1^1D state correlates (together with the X^1S^+ and A^1P states) with the lowest dissociation channel for singlet state, and its $^1S^-$ counterpart with the second singlet channel. Like the 2^1S^+ state (B^1S^+), the diabatic potential curves for the 1^1D and 1^1S^- states cross at larger Be–O separations than those of other species of the same symmetry.

The potential curves for the higher-lying singlet electronic states of BeO have generally complicated forms as a consequence of a number of avoided crossings between the electronic states of bound and predissociative character. They correspond to one-electron excitations into higher-energy virtual orbitals [one of these species represents the third $1p\ 5p$ state of $^1S^+$ symmetry, correlating adiabatically with the non-degenerate $^1S(Be)+^1S(O)$ channel] and to various two-electron excitations. The situation becomes even more complicated if the presence of the states with Rydberg-character are taken into account (Fig. 4). The lowest-lying members of the Rydberg series appear at roughly 55000 cm^{-1} above the ground state. Because of presence of a number of close lying valence-character species, the actual electronic states in this region have a more or less pronounced mixed Rydberg-valence character.

The lowest-lying triplet state of BeO is a^3P , with the main configuration arising by $1p\ 5s$ one-electron excitations. This state has characteristics very similar to its A^1P counterpart. The a^3P state correlates with the lowest-energy dissociation channel $1s^2\ 2s^2$, $^1S(Be) + 1s^2\ 2s^2\ 2p^4$, $^3P(O)$. The second triplet state

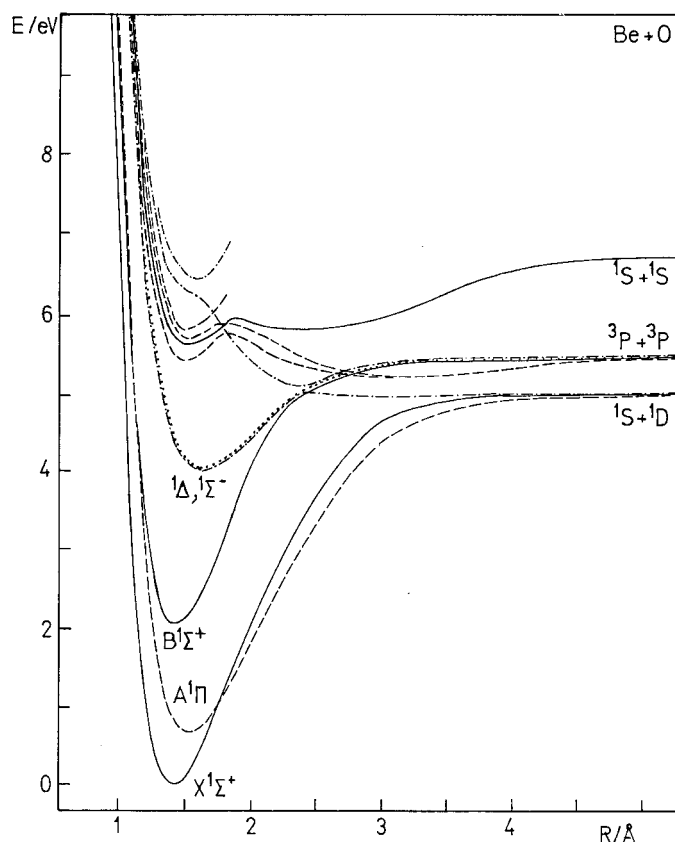


Fig. 5. Potential energy curves for the singlet states of BeO obtained in calculations employing AO basis B (with Rydberg functions). For key to notation see Fig. 3.

is $4s\ 5s\ 5s\ 5s\ b^3\Sigma^+$, the counterpart of the $B^1\Sigma^+$ state. This state correlates with the second channel for triplet species, involving the 3P states of both the beryllium and oxygen atoms. It is followed by $2^3\Sigma^+$, corresponding to the $1p\ 1f\ 2p$ excitation with respect to the ground state electronic configuration and correlating with the $3P(\text{Be}) + ^1D(\text{O})$ states. The $2^3\Sigma^+$ state lies appreciably below its singlet counterpart arising from the same one-electron configuration.

At the equilibrium geometry of the ground electronic state, the next two triplet states in increasing energy order are 1^3D and $1^3\Sigma^-$, both of them stemming from the $1p\ 1f\ 2p$ excitation, as does the $2^3\Sigma^+$. The first of them correlates with the second channel for triplet states. On the other hand, the diabatic potential curve for the $1p\ 1f\ 2p$ configuration crosses at a Be–O distance of about 1.75 Å, the repulsive curve of the $1p^2\ 5s^2$ diabatic species, which results in an avoided crossing of the $1^3\Sigma^-$ and $2^3\Sigma^-$ adiabatic potential curves. This avoided crossing seems to have been overlooked in previous studies.^{23, 24, 30} At larger Be–O distances, the leading

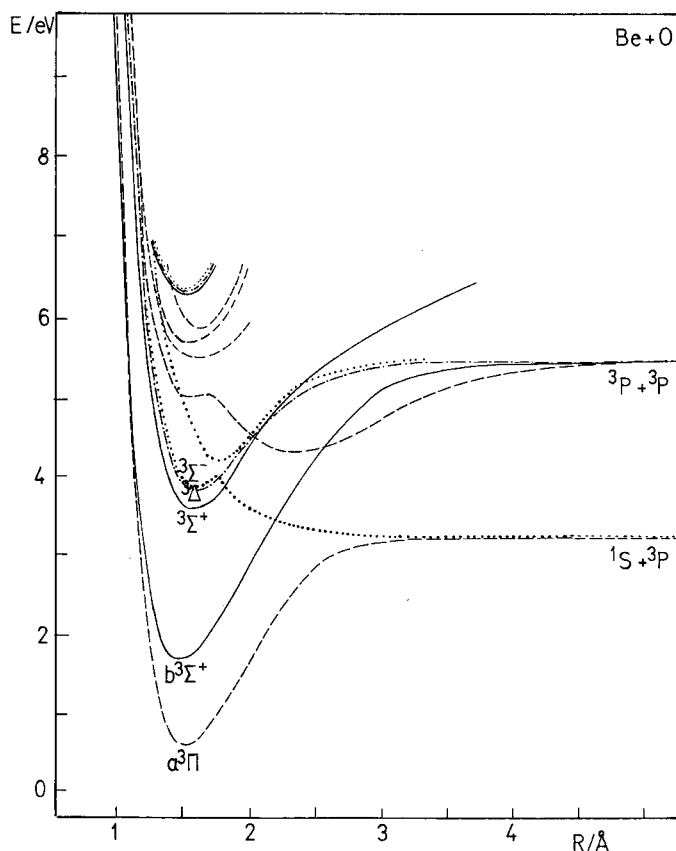


Fig. 6. Potential energy curves for the triplet states of BeO obtained in calculations employing AO basis B (with Rydberg AOs). For key to notation see Fig. 3.

configuration in the 1^3S^- adiabatic state is, thus, $1p^2f1\ 5s^2$; this species correlates with the lowest-lying dissociation channel corresponding to Be and O atoms in their respective ground states. The lowest-lying members of the triplet Rydberg series appear in the same energy region as their singlet counterparts (see Fig. 6).

Relative positions of the dissociation channels computed in the present study are in very good agreement with the experimentally derived values. The electronic configuration of BeO at large atomic separation corresponding to the beryllium atom in its ground state, $1s^2\ 2s^2\ (1S)$, is $2s^2\ 4s^2$. In calculation employing the AO basis A the $1s^2\ 2s\ 2p,\ ^3P$ state of Be is described by the $2s^2\ 4s\ 2p$ and $2s^2\ 4s\ 6s$ configurations [in calculations with the AO basis B, the role of the single $6s$ is taken over by several MOs, among which the $2p_z$ Be orbital is distributed in this case ($6s, 10s, 11s$)]. The $1s^2\ 2s^2\ 2p^4$ configuration of the oxygen atom is described by the $1s^2\ 3s^2\ 1p^4$, $1s^2\ 3s^2\ 1p^3\ 5s$ and $1s^2\ 3s^2\ 1p^3\ 5s^2$ molecular configurations. The electronic configurations involved in the electronic states of BeO which correlate

with the low-energy dissociation channels are obtained by combining these partial configurations with one another.

Vibrational structure of the $B^1S^+ - X^1S^+$ electronic transition

In order to demonstrate the utility of our *ab initio* study for the interpretation of the corresponding spectroscopic measurements, in this subsection the results of calculations of some fine details of the $B^1S^+ - X^1S^+$ electronic spectrum of BeO are presented. The computations of the vibration energy levels and the Franck-Condon factors for the states/transitions in question were carried out employing an approach described elsewhere.⁵⁵ The *ab initio* calculated Franck-Condon factors are presented in Table IV. These results were compared with their counterparts obtained employing the RKR potentials, derived on the basis of experimental findings.⁵⁶ The agreement between the pure theoretical and experimentally derived values is very satisfactory if it is taken into account that the computation of molecular properties, depending explicitly on the forms of the wave functions, is generally less accurate than that for the energy levels. This good agreement is in accordance with the statement above that the results of our *ab initio* calculations, while overestimating the absolute values for the equilibrium Be–O bond length in the electronic states considered, excellently reproduce its relative change upon electronic excitation.

TABLE IV. Comparison of calculated Franck-Condon factors for $B^1S^+(u') - X^1S^+(u'')$ transitions in BeO (upper line) with the corresponding data derived from experimental findings⁵⁶ (lower line)

u''/u'	0	1	2	3	4	5	6	7
0	0.9036 0.8903	0.0902 0.1014	0.0059 0.0079	0.0002 0.0005	0.0000	0.0000	0.0000	0.0000
1	0.0932 0.1056	0.7393 0.7018	0.1514 0.1703	0.0152 0.0205	0.0009 0.0016	0.0000	0.0000	0.0000
2	0.0032 0.0041	0.1628 0.1862	0.6155 0.5556	0.1903 0.2147	0.0261 0.0355	0.0019 0.0037	0.0000	0.0000
3	0.0000	0.0077 0.0106	0.2149 0.2478	0.5238 0.4426	0.2129 0.2407	0.0372 0.0511	0.0034	0.0001
4	0.0000	0.0000	0.0123 0.0183	0.2542 0.2952	0.4572 0.3558	0.2237 0.2532	0.0473	0.0051
5	0.0000	0.0000	0.0000 0.0001	0.0161 0.0263	0.2841 0.3323	0.4101 0.2895	0.2261	0.0561
6	0.0000	0.0000	0.0000	0.0000 0.0001	0.0187 0.0338	0.3070 0.3618	0.3786	0.2228
7	0.0000	0.0000	0.0000	0.0000	0.0000 0.0001	0.0197 0.0404	0.3246	0.3592

The isotope shifts in the $B^1S^+ - X^1S^+$ spectral systems involving ^{16}O and ^{18}O species which was the subject of an experimental study by Bojović *et al.*¹⁰ are presented in Table V. Again, a very reasonable agreement between the theoretical and experimental results can be seen. The analysis presented in this subsection, as

well as that concerning the content of Table III, shows that the results of the present *ab initio* study can serve for the reliable interpretation and prediction of the spectra of the BeO molecule.

TABLE V. Calculated and observed¹⁰ isotope shifts in the $B^1S^+-X^1S^+$ system of BeO. ΔE represent the difference between the term values for the Be¹⁶O and Be¹⁸O bands

$u'-u''$	$\Delta E/\text{cm}^{-1}$ calc.	$\Delta E/\text{cm}^{-1}$ obs.
4-5	-26.8	-31.0
3-4	-27.8	-31.3
2-3	-28.2	-29.6
1-2	-28.2	-29.4
0-1	-27.8	-28.6
4-4	-3.6	-5.4
3-3	-3.6	-4.3
2-2	-3.1	-3.4
1-1	-2.2	-1.0
0-0	-0.9	0.6
5-4	20.1	19.0
4-3	20.6	20.6
3-2	21.5	22.4
2-1	22.9	25.0
1-0	24.7	27.6

CONCLUSION

In this paper, the results of, to our knowledge, the most complete *ab initio* study of the electronic spectrum of BeO are presented. The study involved calculation of all singlet and triplet states in the energy range up to 50000 cm^{-1} . The computations were carried out employing a relatively small AO basis sets and a modest CI treatment; thus the results are of restricted numerical accuracy. On the other hand, they should give a reliable picture of the global structure of the spectrum considered. This is confirmed by the fact that all available experimental findings are reasonably reproduced in our calculations.

Acknowledgements. One of us (M.P.) wishes to thank the Scientific Fund of the Republic of Serbia for financial support. The services and computer time made available by the University in Bonn Computational Center are gratefully acknowledged.

ИЗВОД

Ab initio РАЧУНАЊЕ ЕЛЕКТРОНСКОГ СПЕКТРА BeO

ИВАНА АДАМОВИЋ,* МАЈА ПАРАЏ,* MICHAEL HANRATH** и МИЉЕНКО ПЕРИЋ*

*Факултет за Физичку хемију, Универзитет у Београду, Студентски брз 16, YU-11000 Београд, Југославија
и **Институт за Физичку и Теоријску хемију, Универзитет Бон, Vegelerstrasse 12, D-53115 Бон, СР Немачка

Применом квантохемијског *ab initio* поступка израчуната су нискоенергетска сингулетна и триплетна електронска стања молекула BeO. Установљено је да су сва стања у области енергије између 0 и 50000 cm^{-1} валентног карактера. Посебна пажња посвећена је проучавању дисоцијативног понашања ових стања. Израчуната је вибрациона структура $A^1\P < X^1\S^+ \text{ и } B^1\S^+ < X^1\S^+$ спектралних система.

(Примљено 11. јуна 1999)

REFERENCES

1. A. Lagerqvist, R. Vestö, *Arkiv Mat. Astron. Fysik* **31A** No. 21 (1945)
2. A. Lagerqvist, R. Vestö, *Arkiv Mat. Astron. Fysik* No. 10 (1945)
3. A. Lagerqvist, *Arkiv Mat. Astron. Fysik* **33A** No. 8 (1946)
4. A. Lagerqvist, *Arkiv Mat. Astron. Fysik* **34B** No. 23 (1947)
5. A. Lagerqvist, *Dissertation*, Stocholm (1948)
6. A. Lagerqvist, *Arkiv Fysik* **6** (1953) 141
7. A. Lagerqvist, *Arkiv Fysik* **7** (1954) 473
8. K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand (1979)
9. H. Lavendy, B. Pouilly, J. M. Robbe, *J. Mol. Spectrosc.* **103** (1984) 379
10. V. D. Bojović, A. M. Antić-Jovanović, D. S. Pešić, S. Weniger, *J. Serb. Chem. Soc.* **53** (1988) 669
11. A. Antić-Jovanović, D. S. Pešić, V. Bojović, N. Vukelić, *J. Mol. Spectrosc.* **145** (1991) 403
12. W. A. Chupka, J. Berkowitz, C. F. Giese, *J. Chem. Phys.* **30** (1959) 827
13. R. D. Strivastava, *High Temp. Sci.* **8** (1976) 225
14. K. Shofield, *Chem. Rev.* **67** (1967) 707
15. C. A. Thompson, L. Andrews, *J. Chem. Phys.* **100** (1994) 8689
16. L. Andrews, G. V. Chertihin, C. A. Thompson, J. Dillon, S. Byrne, C. W. Bauschlicher Jr., *J. Phys. Chem.* **100** (1996) 10088
17. C. A. Thompson, L. Andrews, *J. Phys. Chem.* **100** (1996) 12214
18. M. Yoshimine, *J. Chem. Phys.* **40** (1964) 2970
19. G. Verhaegen, W. G. Richard, *J. Chem. Phys.* **45** (1966) 1828
20. W. M. Huo, K. F. Freed, W. Klemperer, *J. Chem. Phys.* **46** (1967) 3556
21. M. Yoshimine, *J. Phys. Soc. Japan* **25** (1968) 1100
22. H. F. Schaefer III, *J. Chem. Phys.* **55** (1971) 176
23. S. V. O'Neil, P. K. Pearson, H. F. Schaefer III, *Chem. Phys. Lett.* **10** (1971) 404
24. P. K. Pearson, S. V. O'Neil, H. F. Schaefer III, *J. Chem. Phys.* **56** (1972) 3938
25. C. W. Bauschlicher Jr., D. R. Yarkony, *J. Chem. Phys.* **72** (1980) 1138
26. C. W. Bauschlicher Jr., B. H. Lengsfeld III, D. R. Yarkony, *J. Chem. Phys.* **73** (1980) 5702
27. H. Partridge, C. W. Bauschlicher Jr., S. R. Langhoff, *Chem. Phys. Lett.* **109** (1984) 446
28. S. R. Langhoff, C. W. Bauschlicher Jr., H. Partridge, *J. Chem. Phys.* **84** (1986) 4474
29. M. Witko, V. Bonačić-Koutecky, *Int. Quant. Chem.* **XXIX** (1986) 1535
30. J. Irisawa, S. Iwata, *Theor. Chim. Acta* **81** (1992) 223
31. K. D. Jordan, R. Seeger, *Chem. Phys. Lett.* **54** (1978) 320

32. Y. Yoshioka, K. D. Jordan, *J. Chem. Phys.* **73** (1980) 5899
33. Y. Yoshioka, K. D. Jordan, *Chem. Phys.* **56** (1981) 303
34. L. Adamowicz, R. J. Bartlett, *J. Chem. Phys.* **83** (1985) 6268
35. P. Pyykko, D. Sundholm, L. Laaksonen, *Mol. Phys.* **60** (1987) 597
36. M. Sana, G. Leroy, *Theor. Chim. Acta* **77** (1990) 383
37. P. W. Fowler, A. J. Sadlej, *Mol. Phys.* **73** (1991) 43
38. G. H. F. Diercksen, A. J., Sadlej, M. Urban, *Chem. Phys.* **158** (1991) 19
39. V. Parasuk, P. Naogra'dy, H. Lischka, M. Urban, *J. Phys. Chem.* **100** (1996) 6325
40. M. Rérat, A. Lichanot, *Chem. Phys. Lett.* **263** (1996) 767
41. B. H. Lengsfeld III, *J. Chem. Phys.* **73** (1980) 382
42. C. W. Bauschlicher Jr., S. R. Langhoff, *Theor. Chim. Acta* **73** (1988) 43
43. S. Polezzo, P. Fantucci, *Theor. Chim. Acta* **73** (1988) 393
44. G. E. Scuseria, T. P. Hamilton, H. F. Schaefer III, *J. Chem. Phys.* **92** (1990) 568
45. L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **94** (1991) 7221
46. E. Clementi, D. W. M. Hofmann, *Int. J. Quant. Chem.* **52** (1994) 849
47. S. Koseki, M. S. Gordon, M. W. Schmidt, N. Matsunaga, *J. Phys. Chem.* **99** (1995) 12764
48. R. J. Buenker, S. D. Peyerimhoff, *Theor. Chim. Acta* **35** (1974) *Theor. Chim. Acta* **39** (1975) 217; R. J. Buenker, S. D. Peyerimhoff, W. Butscher, *Mol. Phys.* **35** (1978) 771; R. J. Buenker, R. A. Philips, *J. Mol. Struct.* **123** (1985) 291; R. J. Buenker, *Int. J. Quant. Chem.* **29** (1976) 435
49. K. Pierloot, B. Dumez, P.-O. Widmark, B. O. Roos, manuscript in preparation
50. B. O. Roos, P. R. Taylor, P. E. M. Siegbahn, *Chem. Phys.* **48** (1980) 157; P. E. M. Siegbahn, J. Almöf, A. Heiberg, B. O. Roos, *J. Chem. Phys.* **74** (1981) 2374
51. M. Hanrath, B. Engels, *Chem. Phys.* **225** (1997) 197
52. S. R. Langhoff, E. R. Davidson, *Int. J. Quant. Chem.* **8** (1974) 61
53. S. Bachkin, J. O. Stoner Jr., *Atomic Energy Levels and Grotrian Diagrams*, North-Holland, Elsevier (1975)
54. C. Sándorfy (Ed.), *The Role of Rydberg States in Spectroscopy and Photochemistry. Low and High Rydberg States*, Kluwer, Dordrecht, The Netherlands (1999)
55. M. Perić, R. Runau, J. Römel, S. D. Peyerimhoff, R. J. Buenker, *J. Mol. Spectros.* **78** (1979) 309
56. S. N. Suchard (Ed.), *Spectroscopic Data, Vol. 1, Heteronuclear Diatomic Molecules*, IFI/Plenum, New York (1975) 218.