Electronic structure of the BaO molecule with dipole moments and ro-vibrational calculations

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A B S T R A C T

The twenty-three low-lying electronic states (singlet and triplet) of the BaO molecule have been studied by using an *ab initio* method. These electronic states have been investigated by using the Complete Active Apace Self-Consistent Field (CASSCF) followed by multi-reference configuration interaction (MRCI + Q) with Davidson correction. The potential energy curves, the internuclear distance R_e, the harmonic frequency ω_e, the rotational constant B_e, the electronic energy with respect to the ground state T_e and the static and transition dipole moment have been investigated. The Einstein spontaneous and induced emission coefficients A_{21} and B_{21}^ω as well as the spontaneous radiative lifetime τ_{spon}, emission wavelength λ_{21} and oscillator strength f_{21} have been calculated by using the transition dipole moment between some doublet electronic states. The calculation of the eigenvalues E_v, the rotational constant B_v, the centrifugal distortion constant D_v, and the abscissas of the turning points R_{min} and R_{max} have been done by using the canonical functions approach. A very good agreement is shown by comparing the values of our work to those found in the literature for many electronic states. Eighteen new electronic states have been studied here for the first time.

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1. Introduction

The barium oxide BaO in gaseous state can be produced either by heating barium carbonate in the presence of coke, carbon black or by thermal decomposition of barium nitrate or other barium salts [1–2]. The barium oxide is a significant component for the application of a thermionic electron emitter. Due to its low work function (1.0–1.3 eV), a large electron current is obtained at relatively low temperatures so that it has been used for cathode-ray tubes [3–4]. In the solid state, the barium oxide can replace lead in the production of optical crown glass since by raising the refractive index, lead oxide raises the dispersive power while barium oxide does not alter it [4]. Moreover, BaO can be used in the reaction of ethylene oxide and alcohols as an ethoxylation catalyst [5]. it can be used as a metal oxide gate to reduce the size of semiconductor devices instead of silicon dioxide (SiO_2) which has a scaling limit of ~1.2 nm due to the leakage of current [6–9]. At the nanoscale, the BaO is mainly used in the formation of nanorods and thin film transistors due to its high performance and stability [10, 11].

Kaufman et al. [12] based on many techniques (Radio-frequency spectroscopy, magnetic deflection, double resonance and microwave resonance) proposed that the ground state for BaO is $X^1\Sigma^+$ and found their spectroscopic constants ω_e, B_e and R_e. Langhoff et al. [13] found the spectroscopic constants (ω_e and R_e) for the state $(1)^3\Pi$. Based on the results of Lagerqvist and Huldt [14–15], Field performed the energy curves and the spectroscopic constants for the ground state $X^1\Sigma^+$ and the first three lowest lying electronic states $(1)^3\Pi$, $(1)^1\Pi$ and $(2)^1\Sigma^+$ [16]. In 1975, he also used the optical–optical double resonance laser spectroscopy for BaO molecule to construct the potential energy curve and to find the vibrational energies and rotational constants of the ground state $X^1\Sigma^+$ [17]. By referring to the spectroscopic constants of the ground state of Field et al. [17], Gottscho et al. [18] used the Optical-Optical Double-Resonance (OODR) spectroscopy to calculate the spectroscopic constants T_e, ω_e, R_e and B_e of the low lying electronic states $(1)^3\Sigma^+$, $(2)^1\Sigma^+$ $(1)^3\Pi$, $(1)^1\Pi$ of the molecule BaO. In addition, they suggested the presence of additional low lying Δ states which perturb the states $(1)^3\Pi$ and $(1)^1\Pi$ and they estimated that $(1)^3\Sigma^+$ is the lowest excited electronic state for the molecule BaO. This estimation is different from all the lighter alkaline earth oxides that have $(1)^3\Pi$ as lowest excited electronic state. One can notice that, most of the theoretical and experimental investigations available in the literature focus on the studies of the ground and few excited electronic states. The experimental electronic structure of the molecule BaO is limited by the high vaporization temperatures and the ease of reduction of their components. Moreover, complications take place in some experiments due to the presence of polymeric species and stable alkaline earth hydroxides [12].

Because of these limited studies for the BaO molecule, more detailed spectroscopic investigations for the higher excited electronic states

would be of a great value for better understanding ~~of~~ the electronic structure of the BaO molecule. In the present work, the potential energy curves for 23 electronic states of BaO molecule are calculated along with the spectroscopic parameters, the static and transition dipole moments, the Einstein coefficients, and the ro-vibrational parameters. A comparison between the energy values T_e for all the alkaline-earth oxides for the different electronic states is presented and discussed. A very good agreement was shown by comparing our results with those available in literature.

2. Method of Calculation

Using the state averaged Complete Active Space Self-Consistent Field (CASSCF) procedure [19–20] followed by a Multireference Configuration Interaction MRDSCI + Q (with Davidson correction) [21–22] the treatment for the electron correlation, the study of the 23 low-lying electronic states of the molecule BrO has been performed. The entire CASSCF configuration space was used as the reference in the MRDSCI calculations, which were done *via* the computational chemistry program MOLPRO [23] by using the advantage of the graphical user interface GABEDIT [24]. This software is designed for high accuracy correlated *ab initio* calculations. With LINUX-type operating system MOLPRO has been run on a PC-computer. The barium atom, with 56

electrons, is treated with effective core potential using the basis set ECP46-MWB for s, p, d and f functions. In this basis, 46 electrons are considered in the effective core potential and 10 electrons are considered as valence electrons. The oxygen species atom, with eight electrons, is treated by using the augmented correlation-consistent basis set aug-cc-pVTZ for s, p and d functions. For these 2 bases and from the 18 electrons for BrO molecule 12 inner electrons are frozen in subsequent calculations so that the remaining six valence electrons are explicitly treated. The corresponding active spaces are $7\sigma(Ba:5d_0, 5d_{2+}, 6p_0, 6s, 7$-$s; O:2p_0, 3s)$, $3\pi(Ba:5d_{\pm1}, 6p_{\pm1}; O:2p_{\pm1})$ and $1\delta(Ba:5d_{2-})$ orbitals in the C_{2v} point group symmetry where the active molecular orbitals are distributed into the irreducible representation a_1, b_1, b_2 and a_2 in the following way $7a_1$, $3b_1$, $3b_2$, $1a_2$ noted [7,3,3,1].

3. Results and Discussion

In the present work, the potential energy curves (PECs) and the permanent dipole moment (PDMs) for 12 singlet and 11 triplet electronic states, in the representation $^{2s+1}\Lambda^{(\pm)}$ of the molecule BaO, have been performed for 135 internuclear distances in the range 1.50 Å ≤ R ≤ 4.20 Å. The energy separation between the lowest and the highest obtained electronic state is 26,865 cm^{-1}. These curves are given in Figs. 1–4 using the basis sets ECP46-MWB, aug-cc-pVTZ for oxygen and barium
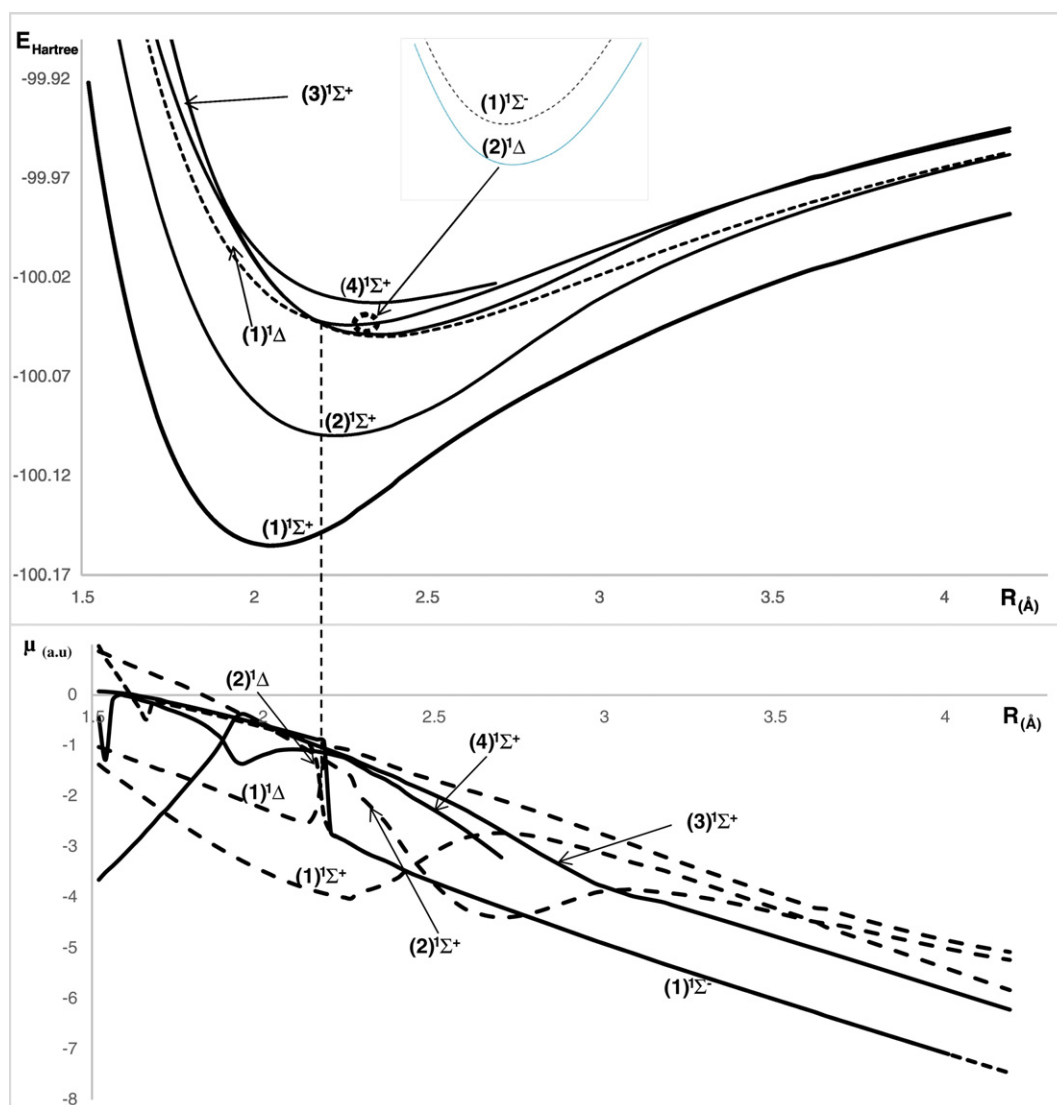

Fig. 1. PECs and DMCs of the singlet electronic $^1\Sigma^{(+/-)}$ and $^1\Delta$-states of BaO molecule. The vertical lines show the agreement between the positions of the avoided crossing of the PECs and the crossings of the DMCs of the corresponding states.