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Electronic structure with dipole moment calculation of the low-lying electronic states of ZnBr molecule

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Adiabatic potential energy curves of 19 low-lying doublet and quartet electronic states in the representation $^{2s+1}\Lambda^{(\pm)}$ of the zinc mono-bromide molecule ZnBr are investigated using high correlated *ab initio* calculations. For the bound states, the equilibrium internuclear distance R_e, the harmonic frequency ω_e, the rotational constant B_e and the electronic transition energy with respect to the ground state T_e have been calculated at the multireference configuration interaction (MRCI) level including single and double excitations with Davidson correction (+Q). Sixteen low-lying states are presented here for the first time. The ground state dissociation energy is also calculated. The comparison between the values of the present work are in agreement with those available in the literature.

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1. Introduction

Although considerable attention has been focused recently on spectroscopic studies concerning small 3d-transition metal compounds, the very short information about the zinc bromide diatomic molecule ZnBr is strongly noticed. In literature, data concerning its low lying electronic states are available for three states only where others are curiously neglected. The early absorption measurements [1] were examined and analyzed by Howell [2] who discussed that the spectra of such zinc halide should result from a $^2\Pi$–$^2\Sigma$ transition in which the 4s electron of Zn in (^{1}S) atomic state is excited to 4p in the (^{3}P) state. The corresponding vibrational frequencies were derived as $\omega'_e = 250\ \text{cm}^{-1}$ and $\omega''_e = 220\ \text{cm}^{-1}$. The questioned value of the ground state vibrational frequency which was nearly equal to the corresponding well-known constant of ZnI at that time motivated subsequent studies using UV emission spectrum ($\omega_e = 312\ \text{cm}^{-1}$) [3] and matrix isolation Raman spectroscopy ($\omega_e = 198\ \text{cm}^{-1}$) [4]. The previous experimental data until 1979 are summarized by Huber and Herzberg [5] giving few information on the $X^2\Sigma^+$ and $C^2\Pi$ states and reporting unclassified bands in the region of $B^2\Sigma^+$ state. However, Rosen [7] presented selected constants for the two low-lying $^2\Sigma^+$ states. Theoretically, only two studies have investigated the electronic structure of ZnBr. Bowmaker and Schwerdtfeger [8] used variety of *ab initio* methods as applied in a modified version of Pople's SCF program to determine the ground state equilibrium bond length R_e, the dissociation energy D_e and the bond force constant k of the diatomic zinc halides. Their values of the ground vibrational frequency of ZnBr molecule range between $253\ \text{cm}^{-1} \leqslant \omega_e \leqslant 275\ \text{cm}^{-1}$. Years later, this radical was studied in the solid state using the relativistic corrected local density functional method [9] from which $R_e = 2.3$ Å and $\omega_e = 268\ \text{cm}^{-1}$ are determined. Among all the above-mentioned studies, yet no investigations have considered the quartet electronic states nor the low excited doublet states higher than $C^2\Pi$. This work uses the *ab initio* method from which the potential energy curves (PECs) and the static dipole moment curves (DMCs) of 19 low-lying doublet and quartet states of ZnBr are presented. The spectroscopic constants as the equilibrium internuclear distance R_e, the harmonic frequency, ω_e the rotational constant B_e and the electronic transition energy with respect to the ground state T_e are calculated for the bound states and the ground state dissociation energy is computed as well. The multiconfigurational approach will be shown to be important in studying the ZnBr molecule due to the strong interactions between its low-lying states and the ionic nature of the ground state.

2. Computational approach of the *ab initio* calculations

Considering the complete active space self consistent field (CASSCF) wave functions as reference, the calculations have been performed using the multi-reference configuration interaction (MRCI) method with Davidson correction (+Q), single and double excitations, as applied in the computational chemistry program

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MOLPRO [10] and taking the advantage of the graphical user interface GABEDIT [11]. The neutral zinc atom with 30 electrons is treated via the energy-consistent ECP10MDF basis set as a system of 10 core electrons where the remaining 20 electrons are described by the energy optimized $(12s12p9d3f2g)/[6s6p4d3f2g]$ valence basis sets [12]. For the neutral bromine atom, the ECP28MWB basis set is employed to treat 28 core electrons and 7 valence electrons are described by the associated $(2s5p)/[2s3p]$ basis sets [13]. Both effective core potentials, ECP28MWB and ECP10MDF, consider relativistic effects where the theoretical level of reference is quasi-relativistic (WB) in the former and relativistic (DF) in the other. The quality of the selected basis sets is checked by comparing our CI calculations for the ground and several excited states of isolated zinc and bromine atoms to the experimental data in NIST Atomic Spectra Database [14]. Among the 65 electrons considered for the zinc mono-halide molecule (30 electrons for Zn and 35 for Br), 38 electrons are treated within the core and the wavefunctions of 27 electrons are to be determined with 19 active molecular orbitals constructed on $3s$, $3p$, $3d$, $4s$, $4p$ and $5s$ of Zn and $4s$, $4p$ and $5s$ of Br. Among these orbitals, the $3s$, $3p$ and $3d$ orbitals of Zn and the $4s$ orbital of Br are kept doubly occupied and frozen in the subsequent calculations so that seven valence electrons are explicitly treated. The active space contains at least 5σ (Zn: $4s$, $4p_0$, $5s$; Br: $4p_0$, $5s$) and 2π (Zn: $4p_{\pm1}$; Br: $4p_{\pm1}$) orbitals in the C_{2v} symmetry group distributed into irreducible representations A_1, B_1, B_2, and B_2 in the following way $5A_1$, $2B_1$, $2B_2$, $0A_2$ noted by [5, 2, 2, 0]. In the range of the internuclear distance R around the equilibrium position of its ground state, the ZnBr molecule is assumed to be mainly ionic. As function of R, the potential energy curves and static dipole moment curves of the doublet and quartet states in the representation of $^{2s+1}\Lambda^{\pm}$ have been calculated for 110 internuclear distances in the range $1.68\ Å \leqslant R \leqslant 4.95\ Å$.

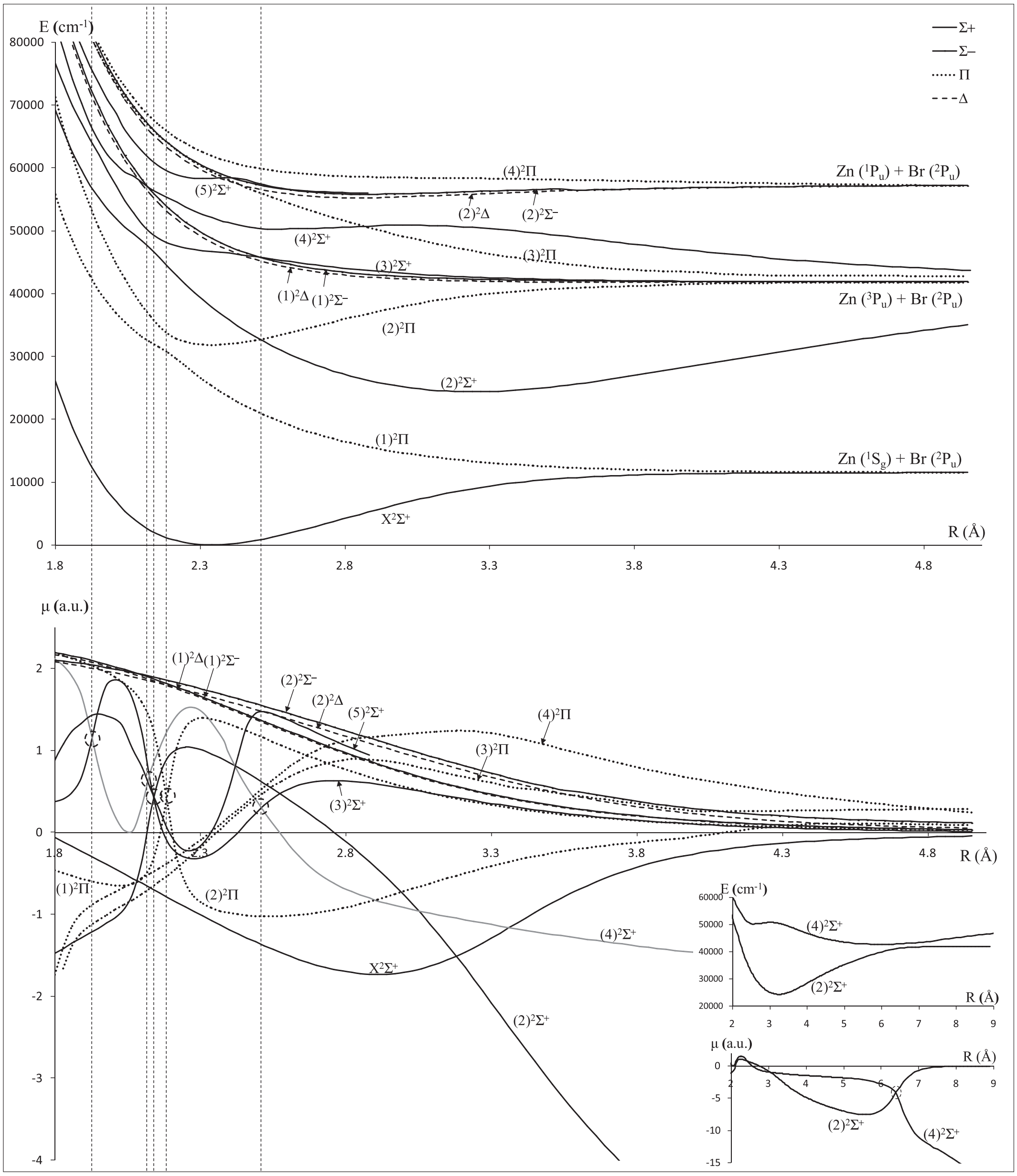

Fig. 1. PECs and DMCs of the doublet electronic states of ZnBr molecule. The vertical lines show the agreement between the positions of the avoided crossing of the PECs and the crossings of the DMCs of the corresponding states.

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