



Electronic structure with the calculation of the rovibrational, and dipole moments of the electronic states of the NaBr and KBr molecules

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ABSTRACT

Due to the lack of the electronic structure of NaBr and KBr diatomic molecules, a systematic investigation of the electronic structure of these molecules was performed using *ab initio* CASSCF/(MRCI + Q) calculations. The adiabatic potential energy curves of the low-lying singlet and triplet electronic states in the representation $2s+1\Lambda^{(+/-)}$ of NaBr and KBr molecules have been investigated. The spectroscopic constants T_e , R_e , ω_e , B_e , the dipole moment μ_e , and the dissociation energies D_e were calculated for the bound states in addition to the percentage ionic character f_{ionic} around the equilibrium position of two electronic states. Moreover, the static and the transition dipole moment curves have been calculated. The nuclear motion study has been performed using the canonical functions approach that allowed the determination of various rovibrational constants E_v , B_v , D_v and the abscissas of the turning points R_{min} and R_{max} for the investigated bound states. The investigated data are in a very good agreement with those given in literature. These results provide effective routes for many industrial applications and for the formation of cold alkali halide molecules in the low-lying vibrational states via experimental techniques.

1. Introduction

Recently, there was a noticeable growing interest in the production of cold and ultracold molecules in which the chemical reactions can be controlled by freezing most degrees of freedom which in turn reduces the decoherence [1–3]. The ability of molecules to interact with each other via magnetic spin-spin forces and electric dipole-dipole allows them to offer new research areas including quantum simulation [4] and high precision measurements [5]. In addition, they possess a wide usage in the molecular dynamics and Bose-Einstein condensate material [6–8]. The alkali halide molecules such as NaBr and KBr were a main interest to the theoretical as well as experimental workers since they have been used in several industrial applications [9,10] and were found to have a noticeable importance as insulators and optical materials [11,12]. Moreover, alkali halide molecules can be used as targets in scintillation detectors and prototype systems for the development of theoretical models and experimental techniques [13]. Also, they can be used as laser window materials, neutron monochromators, infrared prisms, and infrared transmitters [14]. These species are considered fundamentally as promising systems characterized by the ionic bond. It should be taken into consideration that the distribution of charges in diatomic gaseous molecules is very different from that in crystals. In

crystals, the center of all positive charges coincides with that of all negative charges. In other words, an ion is surrounded by other ions in a symmetrical manner. This limits the presence of permanent dipole moment in crystals. On the other hand, in gaseous diatomic molecules a permanent dipole moment, which is necessary to align molecules and reach low vibrational levels [15], is induced due to the separation of the center of positive charge from the center of negative charge [16].

Several experimental and theoretical previous studies in literature were concentrated on the spectroscopic study of the ground state of the alkali halide diatomic molecules including NaBr and KBr [17–33]. For example, a study conducted by Ritner [18] in 1951 where he presented a simple theory of alkali halide gas molecules in the spirit of Born-Mayer lattice theory and calculated the dipole moments and binding energies of alkali halide molecules. In 1953, Barrow and Count [19] have measured the fluctuation bands in the ultraviolet absorption spectra of alkali halides where they determined the upper limits of dissociation energies and some spectroscopic constants for the considered molecules. Later on, Honig et al. [21] have analyzed the data from microwave spectra of alkali halides and measured the internuclear distances, ionic radii, molecular dipole moments and quadrupole coupling constants. In 1957, Rice and Klemperer [22] have measured the infrared spectra of some alkali halide molecules including NaBr and KBr

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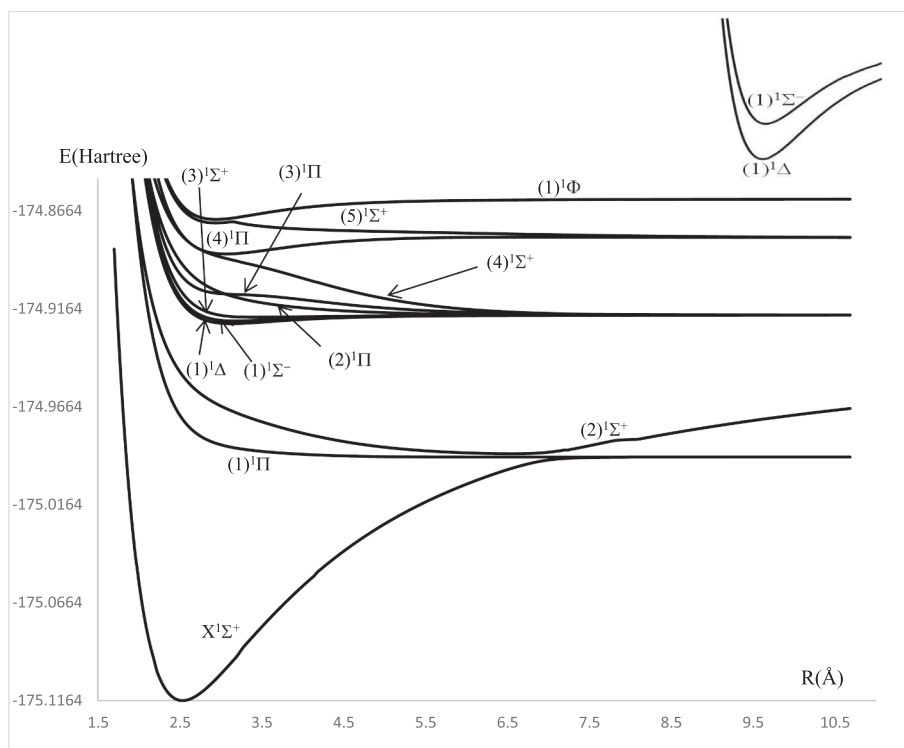


Fig. 1. Potential energy curves of the lowest ${}^1\Sigma^{+/-}$, ${}^1\Pi$ and ${}^1\Delta$ electronic states of the NaBr molecule.

in the gas phase in the region of the fundamental vibration frequency. Later on, the pure rotational spectra of the alkali bromides and the alkali iodides were investigated in the microwave region by Rusk and Gordy in 1962 [23]. Varshni and Shukla [24] proposed the Rittner potential, and a modification of the Rittner potential by including a hyperpolarizability term in order to examine the potential energy functions for alkali halide molecules. In 1974, Matcha and King, Jr [26] used an accurate dipole moment model and provided a deep analysis of the dipole moments of alkali halide molecules. In 2013, the dipole moment, binding energy, rotation-vibration coupling constant and vibrational anharmonicity were calculated by Thakur and Mandal [32] using van der Waals dipole-dipole and dipole-quadrupole interaction and repulsive interaction.

On the other hand, some previous studies were concerned on the analysis of alkali halide molecules in the crystalline phase [34–42]. Most of these studies were concentrated on the electron energy band structure of these molecules where the band gap E_g and electron affinities are determined. The latest study on NaBr and KBr were performed by Ayyash [42] in 2017 in which he calculated theoretically the ionization energies, electron affinities, electronegativities, hardnesses, softness, electrophilic index, HOMO and LUMO energies, and the spectroscopic constants for these molecules using (DFT) level of theory and the basis set 6-311G(d, p).

The lack of studies for the excited electronic states of NaBr and KBr molecules in literature was a strong motivation to analyze deeply the ground and excited electronic states of both molecules in addition to their full spectroscopic and rovibrational study in the present work. For this reason, the *ab initio* method (CASSCF/MRCI + Q) was implemented in order to investigate the potential energy (PECs) and the dipole moment curves (DMCs) of 48 low lying electronic states for these molecules. A spectroscopic analysis was carried out to calculate some spectroscopic parameters including the energy at equilibrium position T_e , the equilibrium bond distance R_e , the harmonic frequency ω_e , the rotational constant B_e , and the rotational vibrational constant α_e . The permanent dipole moment μ_e , the dissociation energy D_e and the percentage ionic character f_{ionic} were also calculated. Moreover, the

transition dipole moment curves have been also investigated among the lowest singlet states. Furthermore, different vibrational levels were investigated for the bound electronic states of NaBr and KBr molecules in which the vibrational energy E_v , the rotational constant B_v , the centrifugal distortion constants D_v , and the abscissas of turning points R_{min} and R_{max} are computed.

2. Computational approach

In order to display the energy levels of NaBr and KBr diatomic molecules, we employed the state averaged Complete Active Space Self Consistent Field (CASSCF) followed by Multireference Configuration Interaction (MRCI) method with Davidson correction (+Q), single and double excitations. In these entire calculations, using the computational chemistry program MOLPRO [43] and taking the advantage of the graphical user interface GABEDIT [44], the CASSCF configuration space was used as the reference in the MRCI calculations. Concerning the basis set, the bromine atom Br of 35 electrons was treated in both molecules as a system of 7 valence electrons and 28 electrons within the core using the effective core potential ECP28MWB basis set [45] for s and p functions. For NaBr molecule, Na atom is treated in all electron scheme using the augmented correlation consistent polarized weighted core valence five zeta (aug-cc-pwCV5Z) given by Peterson [46] for s, p, and d orbitals. On the other hand, the K atom of 19 electrons in KBr molecule was described as a system of 9 valence electrons and 10 electrons in the core by ECP10MWB for s and p orbitals with DGauss-a2-Xfit for d orbital. Therefore, among the 18 electrons considered for NaBr, 12 electrons are frozen for subsequent calculations and 6 valence electrons were explicitly treated. Similarly, 10 electrons out of the 16 electrons considered for KBr are frozen while the 6 remaining electrons were taken as valence electrons. The active space in the C_{2v} symmetry group then contains 6σ (Na: $3s, 3p_0, 3d_0, 3d \pm 2, 4s$; Br: $4p_0$), 3π (Na: $3d \pm 1, 3p \pm 1$; Br: $4p \pm 1$), 1δ (Na: $3d \pm 2$) and 6σ (K: $4s, 4p_0, 3d_0, 3d \pm 2, 5s$; Br: $4p_0$), 3π (K: $3d \pm 1, 4p \pm 1$; Br: $4p \pm 1$) and 1δ (K: $3d \pm 2$) orbitals distributed into the irreducible representation as $6a_1, 3b_1, 3b_2$, and $1a_2$ as [6,3,3,1] for the two molecules.

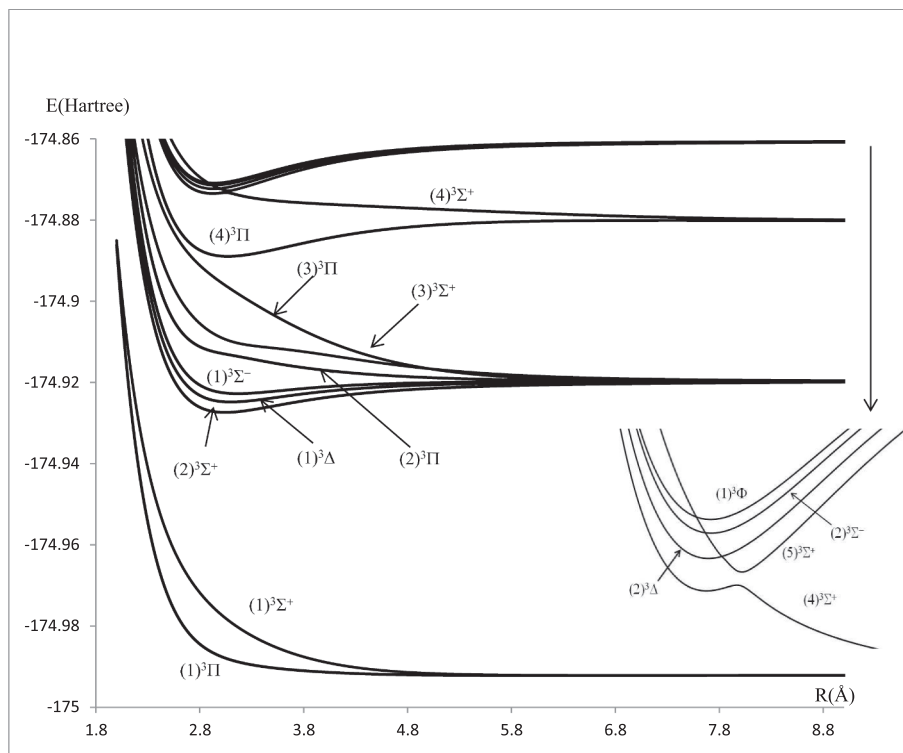


Fig. 2. Potential energy curves of the lowest $^3\Sigma^{+/-}$, $^3\Pi$ and $^3\Delta$ electronic states of the NaBr molecule.

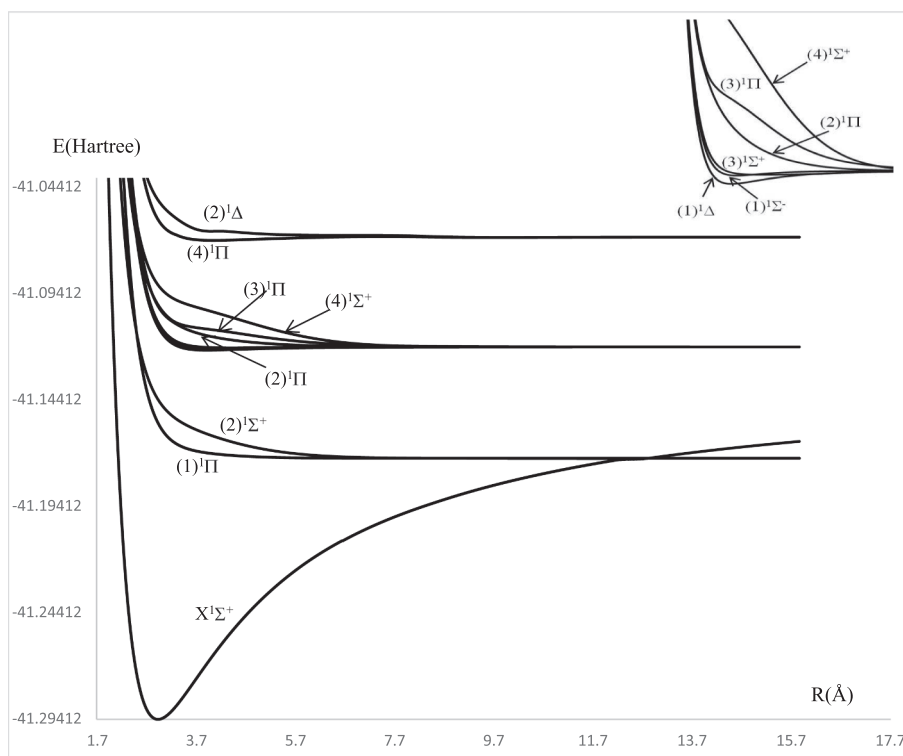


Fig. 3. Potential energy curves of the lowest $^1\Sigma^{+/-}$, $^1\Pi$ and $^1\Delta$ electronic states of the KBr molecule.

3. Results and discussion

3.1. Potential energy curves

Twenty six and twenty two low lying electronic states of singlet and triplet multiplicities corresponding to 6 valence electrons and 13 active

orbitals were investigated for both molecules NaBr and KBr respectively. The potential energies of all the investigated states are plotted as function of internuclear distance R in Figs. 1–4 where the origin is at -175.11635784 Hartree and -41.29412159 Hartree for NaBr and KBr molecules respectively as given in Figs. 1 and 3. The numerical values of these potential energy curves are provided in the [supplementary](#)

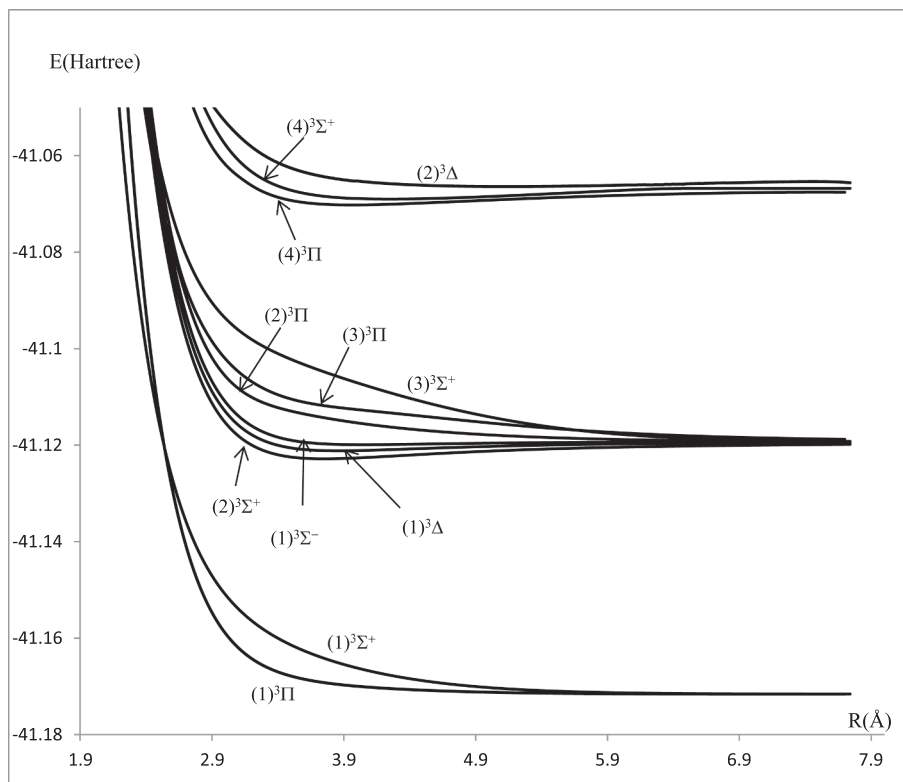


Fig. 4. Potential energy curves of the lowest ${}^3\Sigma^{+/-}$, ${}^3\Pi$ and ${}^3\Delta$ electronic states of the KBr molecule.

Table 1

The lowest dissociation limits of NaBr and KBr molecules.

Dissociation of atomic levels Na + Br	Dissociation energy limit of NaBr levels (cm^{-1})	Molecular states of NaBr	Total dissociation energy limit of Na + Br atoms (cm^{-1})	Relative error (%)
Na ($2p^6 3s, {}^2S$) + Br ($4s^2 4p^5, {}^2P^0$)	0^a	$X^1\Sigma^+, (1)^1\Pi, (1)^3\Sigma^+, (1)^3\Pi$	0^b	0.0
$\text{Na}^+ (2s^2 3p^6, {}^1S) + \text{Br}^- (4s^2 4p^4, {}^1S)$	11432 ^a	$(2)^1\Sigma^+$	12250 ^c	6.6
Na ($2p^6 3p, {}^2P^0$) + Br ($4s^2 4p^5, {}^2P^0$)	15896 ^a	$(3)^1\Sigma^+, (4)^1\Sigma^+, (2)^1\Pi, (3)^1(1)^1\Delta, (1)^1\Sigma^-(2)^3\Sigma^+,$ $(3)^3\Sigma^+, (2)^3\Pi, (3)^3\Pi, (1)^3\Delta, (1)^3\Sigma^-$	16956 ^b	6.3
Na ($2p^6 4s, {}^2S$) + Br ($4s^2 4p^5, {}^2P^0$)	24585 ^a	$(5)^1\Sigma^+, (4)^1\Pi, (4)^3\Sigma^+, (4)^3\Pi$	25739 ^b	4.7
Dissociation limit of atomic levels K + Br	Dissociation energy limit of KBr levels (cm^{-1})	Molecular states of KBr	Total dissociation energy limit of K + Br atoms (cm^{-1})	Relative error (%)
K ($3p^6 4s, {}^2S$) + Br ($4s^2 4p^5, {}^2P^0$)	0^a	$X^1\Sigma^+, (1)^1\Pi, (1)^3\Sigma^+, (1)^3\Pi$	0^b	0.0
$\text{K}^+ (3p^6, {}^1S) + \text{Br}^- (4s^2 4p^4, {}^1S)$	5678 ^a	$(2)^1\Sigma^+$	5830 ^d	2.6
K ($3p^6 4p, {}^2P^0$) + Br ($4s^2 4p^5, {}^2P^0$)	11466 ^a	$(3)^1\Sigma^+, (4)^1\Sigma^+, (2)^1\Pi, (3)^1\Pi, (1)^1\Delta, (1)^1\Sigma^-(2)^3\Sigma^+,$ $(3)^3\Sigma^+, (2)^3\Pi, (3)^3\Pi, (1)^3\Delta, (1)^3\Sigma^-$	12985 ^b	11.7
K ($3p^6 5s, {}^2S$) + Br ($4s^2 4p^5, {}^2P^0$)	22757 ^a	$(4)^1\Pi, (2)^1\Delta, (4)^3\Pi, (2)^3\Delta, (4)^3\Sigma^+$	21534 ^b	5.36

^a Present work.

^b Experimental data from NIST atomic spectra database.

^c Calculated from $\text{IP}(\text{Na}) - \text{EA}(\text{Br})$.

^d Calculated from $\text{IP}(\text{K}) - \text{EA}(\text{Br})$.

material. All the studied electronic states are correlating with the molecular dissociation asymptotes indicated in Table 1. It is noticed that the $(2)^1\Sigma^+$ state in NaBr molecule and the $(2)^1\Sigma^+$ state in KBr molecule are polarized states at the asymptotic limit of dissociation which indicates the dissociation of the molecules into their ionic fragments $\text{Na}^+({}^1S) + \text{Br}^-({}^1S)$ and $\text{K}^+({}^1S) + \text{Br}^-({}^1S)$ respectively. The calculated asymptotic energies are in an acceptable agreement with the experimental energy values of the dissociation asymptote given by NIST atomic spectra database [47]. However, some electronic states are missing in Table 1, in which their absence can be justified by the undulations in the potential energy curves PECs for these electronic states that result from the breakdown of the Born Oppenheimer

approximation, or by the short range electronic interactions at certain energy points which lead to coulomb cusp in the electronic wavefunction.

To discuss the multiplicity of the states it should be kept in mind that the 6 valence electrons comprised by the both molecules, form only singlet and triplet states. Consequently, a doublet alkali earth metal (Na or K) combines with a doublet halide to result in singlet and triplet states of the molecule.

Concerning the type of forces binding the atoms for each of the two molecules, a significant behavior of shallow wells is observed for most electronic states. This behavior is related to the dominance of repulsive forces over the attractive ones for the shallower states within the

Table 2
The spectroscopic parameters for the $X^1\Sigma^+$ and thirteen excited states of NaBr.

State ($^{2S+1}\Lambda$)	T_e (cm^{-1})	R_e (\AA)	ω_e (cm^{-1})	B_e (cm^{-1})	$\alpha_e \times 10^4$ (cm^{-1})	D_e (cm^{-1})	μ_e (a.u.)
$X^1\Sigma^+$	0 ^a	2.539 ^a	293.2 ^a	0.147 ^a	8.79 ^a	27270.21 ^a	3.674 ^a
		2.61 ^b	321.0 ^b				3.480 ^b
		2.502^c		0.1513^c	9.43^c		3.133^c
			302.0^d	0.1495^d	9.39^d		
		2.502^e	298.5^e	0.1513^e	9.42^e		
					10.78 ^f		
					10.47 ^{f1}		
					9.59 ^{f2}		
					8.96 ^{f3}		
					8.86 ^{f4}		
			2.492 ^g		9.44 ^g		
					9.40 ⁱ		
					0.1512^k		
	2.502 ^l	297.5 ^l		9.22 ^l	3.601 ^l		
				8.40 ^m	3.598 ^m		
				9.70 ^{m1}	3.665 ^{m1}		
					3.402 ^{m2}		
					3.472 ^{m3}		
	2.473 ⁿ	306.0 ⁿ			3.968 ^o		
	2.543 ^o	291.9 ^o			3.593 ^{o1}		
					3.586 ^{o2}		
					3.598 ^{o3}		
					3.577 ^{o4}		
					3.588 ^{o5}		
				9.10 ^{p1}	3.685 ^p		
				9.50 ^{p2}			
				9.50 ^{p3}			
				10.80 ^{p4}			
		2.588 ^{q1}	299.1 ^{q1}	0.163 ^{q1}			
		2.586 ^{q2}	300.1 ^{q2}	0.167 ^{q2}			
		2.573 ^{q3}	301.2 ^{q3}	0.169 ^{q3}			
(1) ¹ Π	27256 ^a	6.804 ^a	4.18 ^a	0.020 ^a	5.98 ^a	0.029 ^a	
(2) ¹ Σ^+	27638 ^a	6.550 ^a	58.5 ^a	0.023 ^a	27.75 ^a	2.992 ^a	
(2) ³ Σ^+	41476 ^a	3.046 ^a	109.3 ^a	0.101 ^a	22.28 ^a	0.461 ^a	
(1) ³ Δ	42039 ^a	3.098 ^a	97.1 ^a	0.098 ^a	24.14 ^a	0.599 ^a	
(1) ¹ Δ	42196 ^a	3.137 ^a	93.2 ^a	0.096 ^a	18.04 ^a	0.668 ^a	
(1) ³ Σ^-	42492 ^a	3.167 ^a	82.8 ^a	0.094 ^a	29.45 ^a	0.718 ^a	
(1) ¹ Σ^-	42502 ^a	3.171 ^a	84.2 ^a	0.093 ^a	28.08 ^a	0.731 ^a	
(3) ¹ Σ^+	42919 ^a	3.447 ^a	41.9 ^a	0.079 ^a	62.46 ^a	0.798 ^a	
(4) ³ Π	49911 ^a	3.071 ^a	109.8 ^a	0.100 ^a	16.53 ^a	2.351 ^a	
(4) ¹ Π	49997 ^a	3.067 ^a	110.7 ^a	0.101 ^a	17.88 ^a	2.500 ^a	
(5) ¹ Σ^+	53347 ^a	3.300 ^a	448.9 ^a	0.087 ^a	38.19 ^a	2.007 ^a	
(1) ¹ Φ	53872 ^a	2.942 ^a	134.6 ^a	0.109 ^a	19.13 ^a	0.419 ^a	
(1) ³ Φ	53873 ^a	2.941 ^a	133.2 ^a	0.109 ^a	19.80 ^a	0.416 ^a	

^aPresent work, ^bRef. [18], ^cRef. [21], ^dRef. [22], ^eRef. [23], ^fRef. [24], ^{f1}Ref. [24], ^{f2}Ref. [24], ^{f3}Ref. [24], ^{f4}Ref. [24], ^gRef. [25], ^hRef. [26], ⁱRef. [27], ^jRef. [28], ^kRef. [29], ^lRef. [30], ^mRef. [16], ^{m1}Ref. [16], ^{m2}Ref. [16], ^{m3}Ref. [16], ⁿRef. [36], ^oRef. [31], ^{o1}Ref. [31], ^{o2}Ref. [31], ^{o3}Ref. [31], ^{o4}Ref. [31], ^{o5}Ref. [31], ^pRef. [32], ^{p1}Ref. [32], ^{p2}Ref. [32], ^{p3}Ref. [32], ^{p4}Ref. [32], ^qRef. [42], ^{q1}Ref. [42], ^{q2}Ref. [42], ^{q3}Ref. [42].

The experimental values are indicated in bold.

considered range of internuclear distance. Such dominance seems to be controlled by the type of the employed inner potential for both molecules [48].

A detailed analysis for the $(2)^1\Sigma^+$ in both molecules can be carried out, where in NaBr molecule this state is a bound states that exhibited a minimum at $R = 6.54 \text{ \AA}$ due to the significant avoided crossing of this state with the ground state $X^1\Sigma^+$ at $R = 6.84 \text{ \AA}$. A similar trend goes to the $(2)^1\Sigma^+$ state in KBr molecule, but the avoided crossing is significant between this state and the ground state $X^1\Sigma^+$ at larger internuclear separation of value $R = 12.28 \text{ \AA}$. This large difference in the position of avoided crossing can be explained by the fact that the electronegativity of K is smaller than that of Na ($\chi_K < \chi_{Na}$). Consequently, the

electronegativity difference in KBr molecule is much larger than that of NaBr molecule.

3.2. Spectroscopic parameters

Using the ECPMWB28 with s and p functions only for Br, the spectroscopic constants T_e , R_e , ω_e , B_e , and α_e have been calculated for 14 bound states of NaBr and 11 bound states of KBr molecules by fitting the energy data for these states around their equilibrium position R_e into a polynomial in terms of the internuclear distance. These values are represented in Tables 2 and 3 and compared with the experimental and theoretical data in literature. The values of dissociation energies D_e and

Table 3
The spectroscopic parameters for the $X^1\Sigma^+$ and 11 excited states of KBr.

State ($^{2S+1}\Lambda$)	T_e (cm^{-1})	R_e (\AA)	ω_e (cm^{-1})	B_e (cm^{-1})	$\alpha_e \times 10^4$ (cm^{-1})	D_e (cm^{-1})	μ_e (a.u.)	
$X^1\Sigma^+$	0 ^a	2.937 ^a	196.6 ^a	0.074 ^a	3.93 ^a	22734.91 ^a	4.803 ^a	
		231.0 ^b						
	2.91 ^c		241.0 ^c				4.118 ^c	
			230.0 ^d					
					4.04 ^e			
	2.82 ^f						3.770 ^f	
	2.82 ^h		213.0 ^g	0.081 ^g	4.05 ^g		4.098 ^g	
			219.1 ^h	0.081 ^h				
					4.76 ⁱ			
					4.65 ⁱ¹			
					4.41 ⁱ²			
					3.95 ⁱ³			
					3.88 ⁱ⁴			
	2.83 ^j				4.14 ^j			
							4.173 ^k	
						4.173 ^l		
						4.170 ^m		
				0.081 ⁿ				
2.821 ^o	218.2 ^o			4.06 ^o		4.209 ^o		
				3.70 ^p		4.083 ^p		
				4.20 ^{p1}		4.268 ^{p1}		
						3.972 ^{p2}		
						4.157 ^{p3}		
2.753 ^{q1}	232.0 ^{q1}						4.353 ^f	
2.917 ^f	206.1 ^f						4.273 ^{r1}	
							4.270 ^{r3}	
							4.279 ^{r4}	
							4.265 ^{r5}	
							4.276 ^{r6}	
							4.205 ^s	
				4.03 ^{s1}				
				5.10 ^{s2}				
				3.75 ^{s3}				
				3.50 ^{s4}				
						30729 ^f		
		2.899 ^{u1}	205.0 ^{u1}	0.073 ^{u1}				
		2.896 ^{u2}	206.6 ^{u2}	0.100 ^{u2}				
		2.891 ^{u3}	207.2 ^{u3}	0.112 ^{u3}				
(2) ¹ Σ^+	26540 ^a	12.356 ^a	227.6 ^a	0.420 ^a	0.18 ^a	2088 ^a	22.500 ^a	
(1) ¹ Π	26896 ^a	8.153 ^a	1.7 ^a	0.009 ^a	3.16 ^a	1.24 ^a	0.026 ^a	
(2) ³ Σ^+	37593 ^a	3.750 ^a	48.3 ^a	0.046 ^a	12.28 ^a	658.84 ^a	0.219 ^a	
(1) ³ Δ	37959 ^a	3.859 ^a	38.8 ^a	0.043 ^a	14.29 ^a	349.38 ^a	0.369 ^a	
(1) ¹ Δ	38029 ^a	3.922 ^a	34.5 ^a	0.042 ^a	15.79 ^a	294.13 ^a	0.415 ^a	
(1) ³ Σ^-	38236 ^a	4.056 ^a	26.5 ^a	0.039 ^a	20.21 ^a	127.03 ^a	0.458 ^a	
(1) ¹ Σ^-	38242 ^a	4.059 ^a	25.3 ^a	0.038 ^a	20.85 ^a	120.50 ^a	0.459 ^a	
(3) ¹ Σ^+	38262 ^a	4.797 ^a	8.6 ^a	0.028 ^a	10.89 ^a	87.92 ^a	0.326 ^a	
(4) ³ Π	49142 ^a	3.968 ^a	35.7 ^a	0.041 ^a	7.11 ^a	578.62 ^a	0.009 ^a	
(4) ¹ Π	49343 ^a	4.050 ^a	30.7 ^a	0.039 ^a	12.53 ^a	322.81 ^a	0.159 ^a	
(4) ³ Σ^+	49411 ^a	4.252 ^a	28.9 ^a	0.036 ^a	7.69 ^a	486.42 ^a	0.611 ^a	

^aPresent work, ^bRef. [17], ^cRef. [18], ^dRef. [19], ^eRef. [20], ^fRef. [21], ^{g1}Ref. [21], ^{g2}Ref. [21], ^{g3}Ref. [21], ^{g4}Ref. [21], ^{g5}Ref. [22], ^hRef. [23], ⁱRef. [24], ⁱ¹Ref. [24], ⁱ²Ref. [24], ⁱ³Ref. [24], ⁱ⁴Ref. [24], ^jRef. [25], ^kRef. [26], ^lRef. [27], ^mRef. [28], ^{m1}Ref. [28], ^{m2}Ref. [28], ^{m3}Ref. [28], ⁿRef. [29], ^oRef. [30], ^{o1}Ref. [30], ^{o2}Ref. [30], ^{o3}Ref. [30], ^{o4}Ref. [30], ^{o5}Ref. [30], ^pRef. [16], ^{p1}Ref. [16], ^{p2}Ref. [16], ^{p3}Ref. [16], ^qRef. [36], ^rRef. [31], ^{r1}Ref. [31], ^{r2}Ref. [31], ^{r3}Ref. [31], ^{r4}Ref. [31], ^{r5}Ref. [31], ^{r6}Ref. [31], ^sRef. [32], ^{s1}Ref. [32], ^{s2}Ref. [32], ^{s3}Ref. [32], ^{s4}Ref. [32], ^rRef. [33], ^rRef. [42], ^{u1}Ref. [42], ^{u2}Ref. [42], ^{u3}Ref. [42]. The experimental values are indicated in bold.

the dipole moments of the considered electronic states at their equilibrium position R_e are also provided. While the absence of the spectroscopic constants for some electronic states is justified by the presence of crossing or avoided crossing between electronic states of same type belonging to same symmetry.

A comparison of our calculated spectroscopic constants was carried out based on the data found experimentally or theoretically by using

Table 4
Study of the trend of the spectroscopic constants of the different electronic states of the molecules NaBr and KBr.

State	constants	NaBr	KBr	trend
$X^1\Sigma^+$ Ground State	T_e (cm^{-1})	0.0	0.0	
	R_e (\AA)	2.539	2.937	↗
	ω_e (cm^{-1})	293.2	196.6	↘
	B_e (cm^{-1})	0.147	0.074	↘
(1) ¹ Π	T_e (cm^{-1})	27,256	26,896	↘
	R_e (\AA)	6.804	8.153	↗
	ω_e (cm^{-1})	4.18	1.7	↘
	B_e (cm^{-1})	0.020	0.009	↘
(2) ³ Σ^+	T_e (cm^{-1})	41,476	37,593	↘
	R_e (\AA)	3.046	3.750	↗
	ω_e (cm^{-1})	109.3	48.3	↘
	B_e (cm^{-1})	0.101	0.046	↘
(1) ³ Δ	T_e (cm^{-1})	42,039	37,959	↘
	R_e (\AA)	3.098	3.859	↗
	ω_e (cm^{-1})	97.1	38.8	↘
	B_e (cm^{-1})	0.098	0.043	↘
(1) ¹ Δ	T_e (cm^{-1})	42,196	38,029	↘
	R_e (\AA)	3.137	3.922	↗
	ω_e (cm^{-1})	93.2	34.5	↘
	B_e (cm^{-1})	0.096	0.042	↘
(1) ³ Σ^-	T_e (cm^{-1})	42,492	38,236	↘
	R_e (\AA)	3.167	4.059	↗
	ω_e (cm^{-1})	82.8	26.5	↘
	B_e (cm^{-1})	0.094	0.039	↘
(1) ¹ Σ^-	T_e (cm^{-1})	42,502	38,242	↘
	R_e (\AA)	3.171	4.059	↗
	ω_e (cm^{-1})	84.2	25.3	↘
	B_e (cm^{-1})	0.093	0.038	↘
(3) ¹ Σ^+	T_e (cm^{-1})	42,919	38,262	↘
	R_e (\AA)	3.447	4.797	↗
	ω_e (cm^{-1})	41.9	8.6	↘
	B_e (cm^{-1})	0.079	0.028	↘
(4) ³ Π	T_e (cm^{-1})	49,911	49,142	↘
	R_e (\AA)	3.071	3.968	↗
	ω_e (cm^{-1})	109.8	35.7	↘
	B_e (cm^{-1})	0.100	0.041	↘
(4) ¹ Π	T_e (cm^{-1})	49,997	49,343	↘
	R_e (\AA)	3.067	4.050	↗
	ω_e (cm^{-1})	110.7	30.7	↘
	B_e (cm^{-1})	0.101	0.039	↘

different models. Our calculated values of the equilibrium bond length R_e are relatively consistent with those in literature with relative difference 0.3% [31] $\leq \Delta R_e / R_e \leq 2.9\%$ [18] and 0.9% [31] $\leq \Delta R_e / R_e \leq 6.4\%$ [36] for NaBr and KBr molecules respectively. Our calculated value of the harmonic frequency ω_e of NaBr molecule agrees with the majority of values reported in literature with the discrepancy 0.4% [31] $\leq \Delta \omega_e / \omega_e \leq 4.4\%$ [36]. Exception is significant for the value reported by Rittner [18] where the relative discrepancy reaches 8.6%. While for KBr molecule, an acceptable agreement is achieved upon the comparison of the harmonic frequency values where the relative error is of minimum value 3.9% when compared with the value calculated by Ayash [42] via density functional theory and using 6 -311 + +G (df, pd) basis set. A noticeable deviation from our value of the harmonic frequency occurs for those given by Levi [17], Ritner [18], Barrow and Caunt [19], where the relative discrepancies reach 14.7%, 18.3% and 14.3% respectively. Concerning the values of B_e , it is noted that our calculated ones are generally compatible with those given in literature with relative error approximately equal to 2.6% and 8.6% for most the reported values corresponding to NaBr and KBr respectively with a significant exception

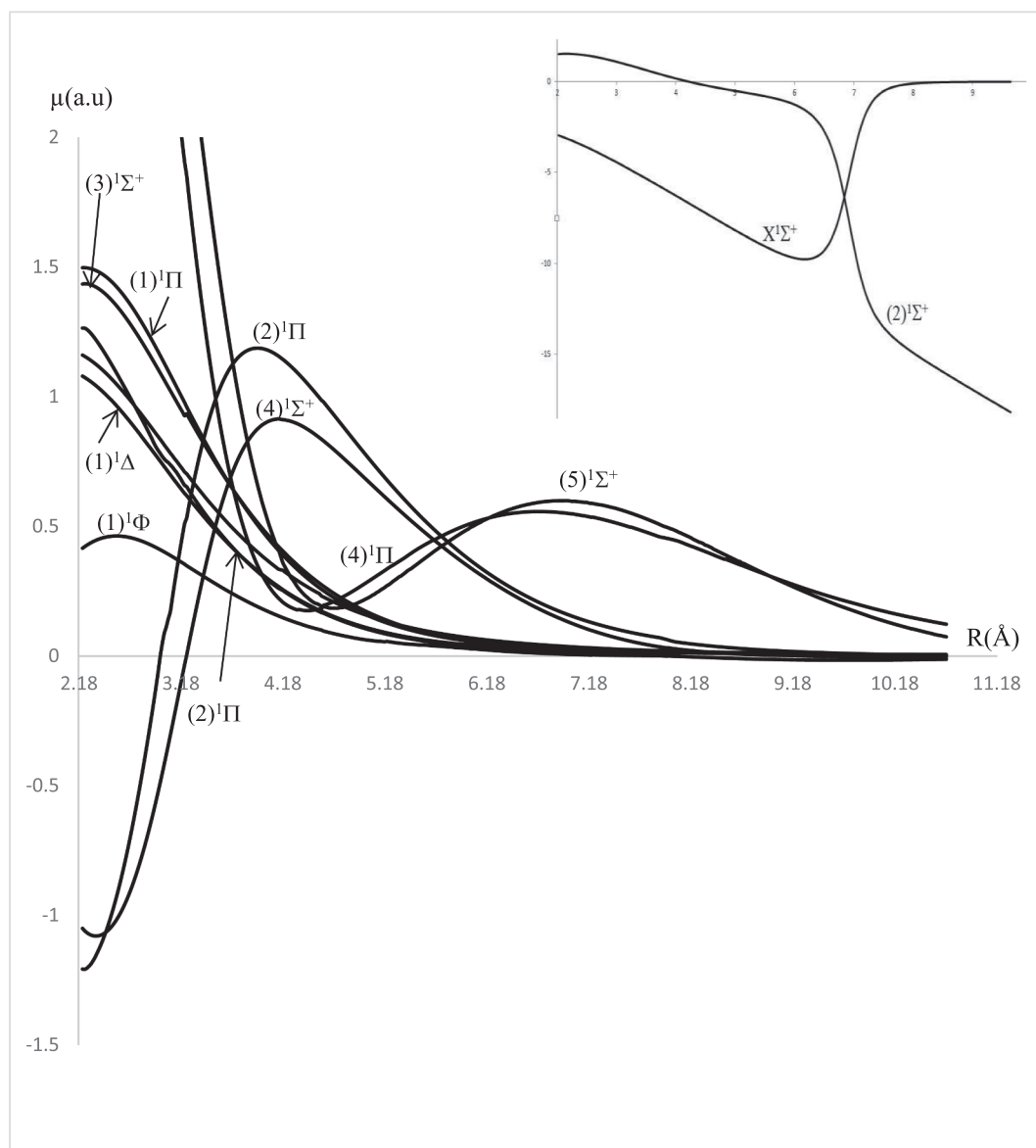


Fig. 5. Permanent dipole moment curves of the lowest ${}^1\Sigma^{+/-}$, ${}^1\Pi$ and ${}^1\Delta$ electronic states of the NaBr molecule.

noticed for those reported by Ayash [42].

One can find a good agreement for the value of the rotational constant α_e with average relative difference 7.7% for NaBr and 7.3% for KBr. The trend of the calculated spectroscopic constants of the investigated electronic state of both molecules was studied and given in Table 4. The right trend of these spectroscopic constants can be considered as a confirmation of the reliability of the present work.

Also the spectroscopic constants of the ground state are also calculated for both molecules when using ECP28MWB with s and p functions and introducing d polarization function from aug-ccpVTZ and aug-cc-pwCV5Z in order to discuss the effect of d function. These calculated values are given Table TS1 in the supplementary material where the potential energy curves with these basis set are given in Figures (FS1 and FS2) in the supplementary material for NaBr and KBr respectively.

Upon the comparison of the spectroscopic constants of the ground state with the experimental values given by Rice and Klemperer [22], one can find that the average relative differences between the experimental data given in the Table TS1 and the spectroscopic values

obtained using ECP28MWB with s and p functions only are 3.6% and 6.4% for NaBr and KBr respectively. While these relative differences become 2.8% and 5.7% for NaBr and KBr respectively when introducing d polarization function in the basis of Br atom. This d polarization function is added from the basis set aug-ccpVTZ. On the other hand, introducing this function from this basis set leads to a shift around the equilibrium bond length of the $(1)^\Delta$ and $(3)^\Sigma^+$ states as shown in Fig. FS2 in the supplementary material.

However, introducing a d polarization function to the basis of Br from aug-cc-pwCV5Z results in an average relative difference of 2.5% for NaBr with the experimental data reported by Rice and Klemperer, [22] while this relative difference becomes 12.2% for KBr which is relatively large.

3.3. Permanent dipole moment and ionic character f_{ionic}

The dipole moment possesses a useful impact in the construction of molecular orbitals based model of bonding. Additionally, it can be

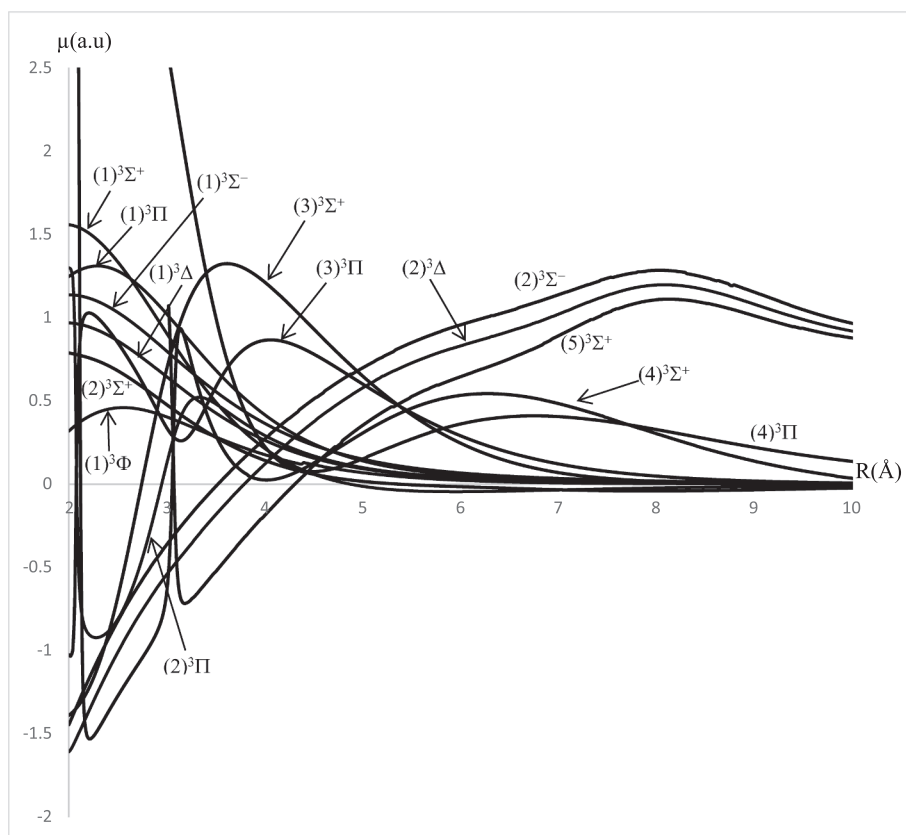


Fig. 6. Permanent dipole moment curves of the lowest ${}^3\Sigma^{+/-}$, ${}^3\Pi$ and ${}^3\Delta$ electronic states of the NaBr molecule.

utilized to find the strength of long range dipole-dipole forces and understand the macroscopic properties of imperfect gas, solid and liquid [49,50]. Due to their importance, the dipole moment curves (DMCs) of the investigated electronic states of NaBr and KBr molecules have been investigated and plotted as function of internuclear separation R as shown in Figs. 5–8 where Na and K atoms are taken at origin in both molecules. Thus, a negative value of the dipole moment indicates the reversed polarity $\text{Na}^{\delta+} \text{Br}^{\delta-}$, and $\text{K}^{\delta+} \text{Br}^{\delta-}$. On the other hand, a positive dipole moment reveals a charge transfer from Na to Br and from K to Br.

One can notice the agreement of the position of avoided crossing between two electronic states with their corresponding positions of crossing in the DMCs. This agreement confirms the accuracy and validity of our results. These positions are the main reason of reversing the polarities of the atoms and interchanging the electronic characteristics.

The correct behavior of molecules that dissociate into neutral atoms at the asymptotic limit of dissociation is observed via the common trend of the most electronic states of NaBr and KBr molecules where the PDM of these electronic states smoothly approaches zero at these limits. Exception goes to the states discussed previously, the $(2)^1\Sigma^+$ state of NaBr molecule and the $(2)^1\Sigma^+$ state of KBr molecule where their dipole moments tend to a constant value at the asymptotic limits of dissociation. A deeper analysis of these states will be provided in the spirit of specifying the bond nature between atoms.

The DMC of the $(2)^1\Sigma^+$ state of NaBr molecule has an ionic character at the asymptotic limit of dissociation. While at smaller internuclear separations this ionic character seems to be mixed with a covalent character. In reverse, the $X^1\Sigma^+$ state of this molecule is of covalent character at its dissociation limit and of mixed character at smaller internuclear separations where its DMC presents negatively

increased values with largest magnitude $|\mu| = 9.77$ a.u. at $R = 6.14$ Å. While the $(2)^1\Sigma^+$ state of KBr exhibits a positive value over the range $1.8\text{Å} < R < 5.12\text{Å}$ and tends to zero over $5.14\text{Å} < R < 11.96\text{Å}$. Then, its absolute value abruptly increases negatively at $R = 11.98\text{Å}$ where the ionic character dominates the covalent one beyond this range of R till reaching a maximum value $|\mu| = 26.28$ at $R = 14.26\text{Å}$. Concerning the ground state of KBr, there is a significant ionic character of this state with no covalent character within the range $1.8\text{Å} < R < 11.96\text{Å}$ since its DMC is linearly decreasing over all this range of internuclear separation. While, a covalent character slightly mixes into the ionic character within a very small range of R till the dipole moment tends to zero at the asymptotic limit of dissociation which is a sign of covalent character and dissociation into neutral fragments. In order to confirm the characters discussed above, the percentage ionic character have been calculated using the formula [51] $f_{\text{ionic}} = \frac{\mu_{\text{e}}}{eR_{\text{e}}}$ for the mentioned electronic states. For the ground state $X^1\Sigma^+$, the ionicity is found to be $f_{\text{ionicity}} = 0.76$, and 0.73 which correspond to 76% and 73% for NaBr and KBr molecules respectively. For the $(2)^1\Sigma^+$, the ionicity fraction is $f_{\text{ionicity}} = 0.24$, and 0.96 which correspond also to 24% and 96% for NaBr and KBr molecules respectively. This is a kind of evidence about the dominance of ionic bond over the covalent bond around the equilibrium position in the ground state for both molecules. A covalent bond is dominant for the $(2)^1\Sigma^+$ state in NaBr molecule around its equilibrium position. In contrast, this state in KBr molecule is of purely ionic character around the equilibrium position which explains the presence of an ionic bond, where the electrons transfer to the Br atom of large electronegativity from the K atom which has much smaller electronegativity than that of Br and Na.

The absolute values of the permanent dipole moment of the ground state at equilibrium bond length are found to be 3.674 a.u. and 4.803 a.u.

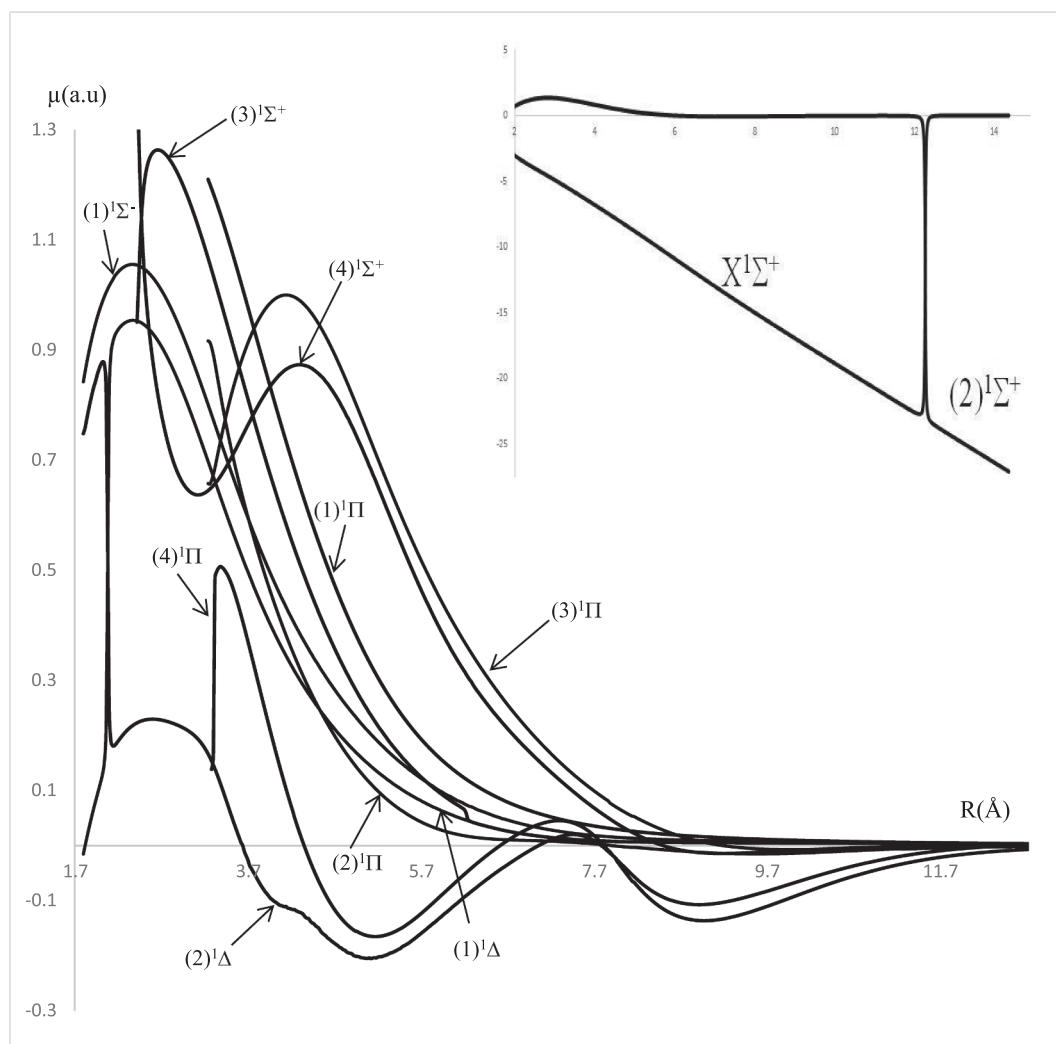


Fig. 7. Permanent dipole moment curves of the lowest ${}^1\Sigma^{+/-}$, ${}^1\Pi$ and ${}^1\Delta$ electronic states of the KBr molecule.

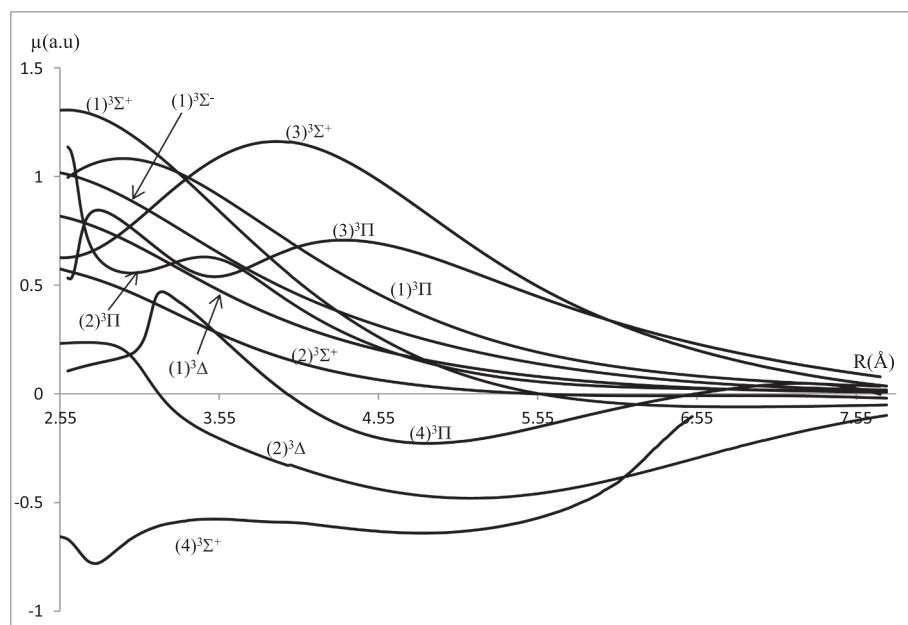


Fig. 8. Permanent dipole moment curves of the lowest ${}^3\Sigma^{+/-}$, ${}^3\Pi$ and ${}^3\Delta$ electronic states of the KBr molecule.

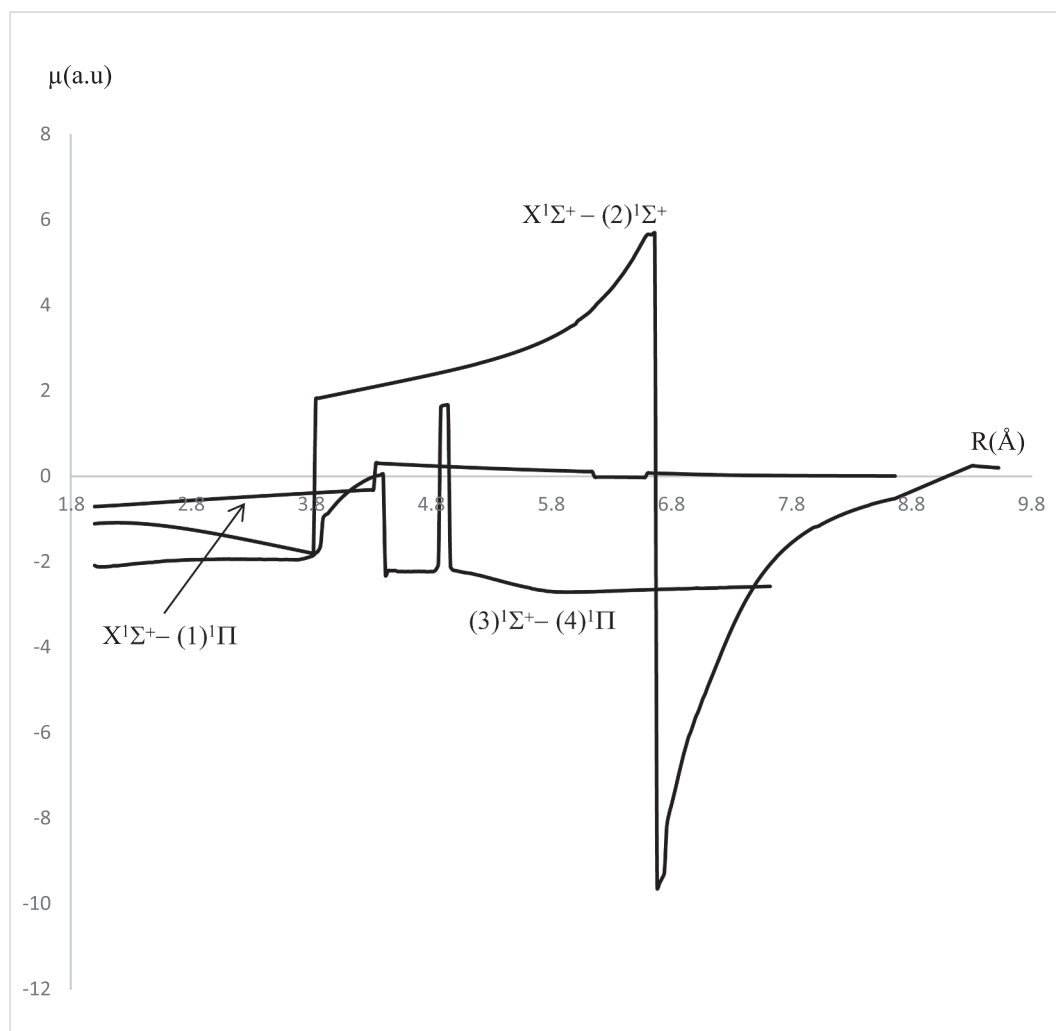


Fig. 9. The allowed transition dipole moment curves of NaBr molecules.

for NaBr and KBr respectively. Those values show a very good agreement with the values reported in literature. The most close value of the dipole moment corresponding to the ground state of NaBr is that given by Kumar and Shanker [16] where there is a small relative error of 0.2%. The dipole moment of the ground state has an average relative error of 3.8%. On the other hand, the dipole moment corresponding to KBr slightly deviates from those in literature with average relative error of 13.2%.

3.4. The transition dipole moments

The production of stable ultracold molecules is a challenging process that requires a deep analysis of the allowed electronic transitions in diatomic molecules. Thus the transition dipole moment curves (TDMCs) of the transitions $X^1\Sigma^+-(2)^1\Sigma^+$, $X^1\Sigma^+-(1)^1\Pi$, $X^1\Sigma^+-(3)^1\Sigma^+$ and $(3)^1\Sigma^+-(4)^1\Pi$ are plotted as function of internuclear distance R and represented in Figs. 9 and 10. The negative values of TDM are related to the switching of the electronic motion from one electronic state to another and the mixing of the wavefunctions of these states. The TDMCs of $X^1\Sigma^+-(1)^1\Pi$ and $X^1\Sigma^+-(2)^1\Sigma^+$ vanish in both molecules at large internuclear distance. This behavior can be clarified by the spin forbidden transitions between atomic orbitals at asymptotic limits. The TDMCs of the $(3)^1\Sigma^+-(4)^1\Pi$ transition tend to constant values which equal to

2.574 a.u. and 2.780 a.u. for NaBr and KBr respectively. From these values, the line strength S is calculated and found to be 13.3 s^{-1} for NaBr and 15.5 s^{-1} for KBr. These values are compared to the experimental values reported in the NIST atomic spectra database, where for NaBr $S = 12.8 \text{ s}^{-1}$ and for KBr $S = 15.0 \text{ s}^{-1}$.

Also the theoretical values of the oscillator strength f corresponding to $(3)^1\Sigma^+-(4)^1\Pi$ transition are $f = 0.14$ and $f = 0.25$, where the experimental ones are 0.17 and 0.18 for NaBr and KBr respectively.

Similarly for the $X^1\Sigma^+-(3)^1\Sigma^+$ transition of KBr, the transition dipole moment value is $\mu = 2.788$ a.u. Thus, the theoretical values of S and f are 15.5 s^{-1} and 0.89 respectively where the experimental values are 16.9 s^{-1} and 0.33.

Thus, a good agreement is verified between the values calculated in the present work and the experimental values in the NIST atomic spectra database.

3.5. The ro-vibrational calculations

Using the canonical function approach [52–54] and cubic spline interpolation between each two consecutive points of the potential energy curve, a rovibrational study has been carried in order to induce different vibrational transitions. Thus, the vibrational energy E_v , the rotational constant B_v , and the centrifugal distortion constant D_v , and

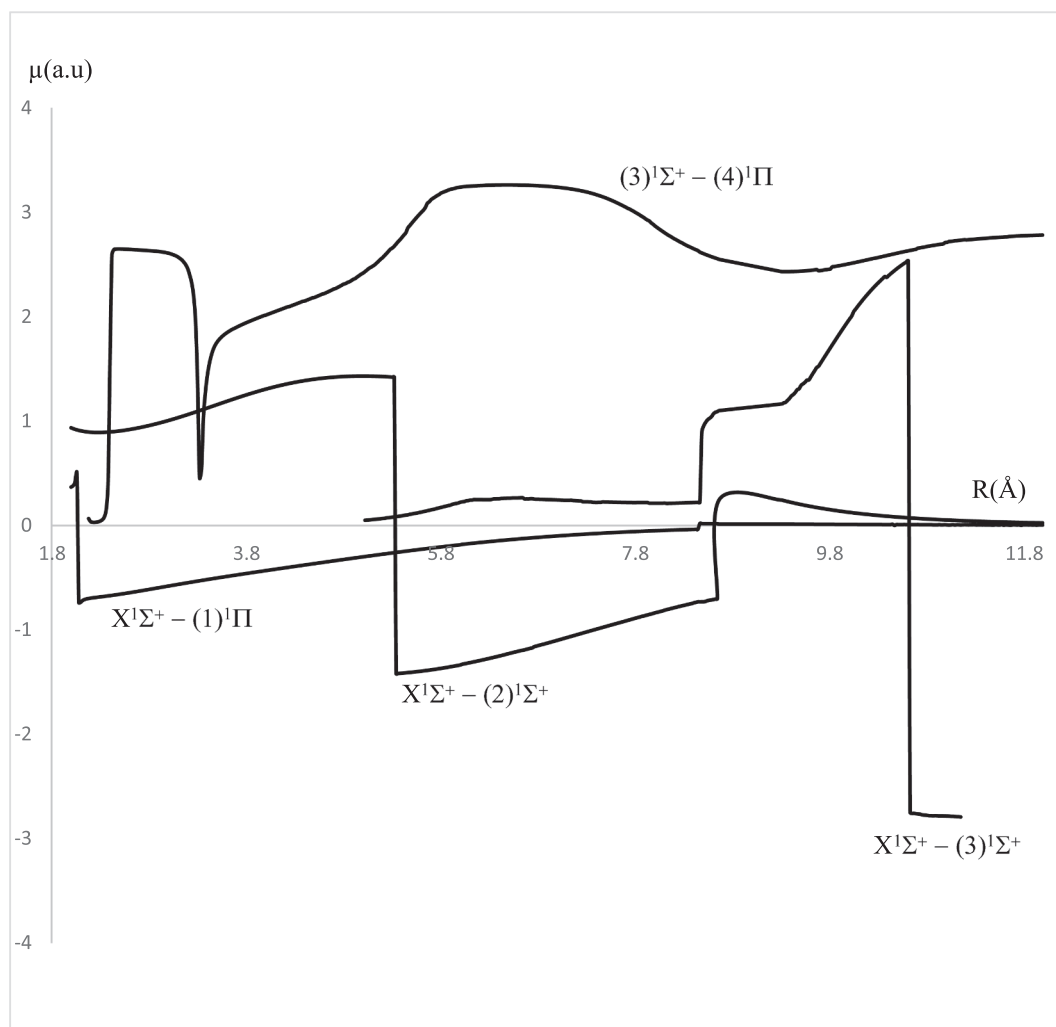


Fig. 10. The allowed transition dipole moment curves of KBr molecules.

Table 5

Values of the vibrational energies, the rotational constants and the abscissas of the turning points for the different vibrational levels of $X^1\Sigma^+$ of NaBr molecule.

v	E_v	$B_v(\times 10^1)$	$D_v(\times 10^7)$	R_{\min}	R_{\max}
0	146.31	1.465	1.47671	2.548	2.619
1	436.99	1.456	1.47635	2.406	2.686
2	725.28	1.447	1.47642	2.373	2.735
3	1011.18	1.438	1.47570	2.346	2.776
4	1294.71	1.430	1.47594	2.325	2.814
5	1575.85	1.421	1.47470	2.306	2.848
6	1854.66	1.412	1.47259	2.289	2.881
7	2131.14	1.403	1.46847	2.274	2.912
8	2405.33	1.395	1.45718	2.260	2.942
9	2677.29	1.386	1.43624	2.247	2.971
10	2947.14	1.376	1.40132	2.235	2.999
11	3215.02	2.012	1.63263	2.224	3.026

the abscissas of the turning point R_{\min} and R_{\max} for each vibrational level were determined for the ground state of NaBr and KBr and reported in Tables 5 and 6, whereas those of some excited electronic states have been provided in Tables TS2 and TS3 in the supplementary material.

The absence of vibration rotation calculation for the other electronic states corresponds either to very shallow states or to the presence of crossing or avoided crossing between electronic states.

4. Conclusion

A spin free study was performed to investigate the potential energy curves and dipole moment curves of twenty six and twenty two singlet and triplet electronic states for the molecules sodium bromide NaBr and potassium bromide KBr respectively by implementing MCSCF/MRCI technique and employing the ECP28MWB basis set for Br atom, and aug-cc-pwCV5Z for Na atom. For K atom, ECP10MWB was used for s and p orbitals with DGauss-a2-Xfit for d. By interpolating points around the minimum of the potential energy curves, the spectroscopic constants (T_e , R_e , ω_e , B_e , α_e) in addition to the dissociation energy D_e and the dipole moment at the equilibrium position μ_e have been calculated for the bound states of NaBr and KBr molecules. Upon the comparison of these spectroscopic parameters with the previous data in literature, a good consistency of calculated results was achieved. This is in agreement with our previously published work, using the same calculation method [55–60].

The percentage ionic character f_{ionic} was also calculated for the ground state $X^1\Sigma^+$ and the $(2)^1\Sigma^+$ state of both molecules around the

Table 6

Values of the vibrational energies, the rotational constants and the abscissas of the turning points for the different vibrational levels of $X^1\Sigma^+$ of KBr molecule.

$(X)^1\Sigma^+$	E_v	$B_v(\times 10^1)$	$D_v(\times 10^8)$	R_{\min}	R_{\max}
0	103.06	0.742	4.25182	2.859	3.021
1	298.75	0.738	4.28852	2.807	3.088
2	492.58	0.735	4.23231	2.773	3.173
3	685.27	0.731	4.31322	2.746	3.178
4	876.24	0.727	4.22118	2.724	3.216
5	1066.02	0.723	4.30267	2.705	3.250
6	1254.26	0.719	4.26957	2.688	3.282
7	1441.10	0.716	4.21025	2.672	3.313
8	1810.71	0.708	4.15350	2.645	3.370
9	1993.58	0.704	4.33824	2.633	3.398
10	2174.95	0.700	4.33129	2.622	3.425
11	2354.85	0.696	4.11846	2.611	3.451
12	2533.63	0.693	4.44128	2.601	3.477
13	2710.84	0.689	4.22361	2.592	3.502
14	2886.78	0.685	4.13068	2.582	3.527
15	3061.56	0.681	4.49542	2.574	3.511
16	3234.79	0.678	4.14836	2.566	3.575
17	3406.84	0.674	4.13300	2.558	3.599
18	3577.72	0.670	4.51971	2.551	3.623
19	3747.11	0.667	4.12906	2.543	3.646
20	3915.33	0.663	4.08853	2.537	3.669
21	4082.43	0.660	4.52085	2.530	3.692
22	4248.08	0.656	4.18069	2.523	3.715
23	4412.56	0.652	4.00487	2.517	3.738
24	4575.96	0.649	4.46494	2.511	3.760
25	4738.01	0.646	4.30234	2.505	3.782
26	4898.82	0.642	3.94379	2.499	3.805
27	5058.60	0.638	4.30676	2.491	3.827
28	5217.14	0.635	4.43483	2.489	3.849
29	5374.41	0.632	4.00387	2.484	3.871

equilibrium position. A dominance of the ionic character over the covalent character was confirmed for the $X^1\Sigma^+$ of NaBr and KBr. The $(2)^1\Sigma^+$ state of NaBr is of covalent nature around R_e while this state in KBr has a strong ionic character. Additionally, the transition dipole moments are calculated for the molecules NaBr and KBr and the canonical function approach and cubic spline interpolation allowed the calculation of the ro-vibrational constants E_v , B_v , D_v with the abscissas of turning points R_{\min} and R_{\max} different vibrational levels of the ground state and some low lying electronic states of the NaBr and KBr molecules.

Appendix A. Supplementary data

Given in Figs. FS1 and FS2 the potential energy curves of the ground state and first two excited states of NaBr and KBr respectively investigated using ECP28MWB basis set for Br with s, p functions and introducing d polarization function from aug-ccpVTZ and aug-cc-pwCV5Z with their spectroscopic constants given in Table TS1.

In Tables TS2 and TS3 in the supplementary material SM1 we provided the values of the eigenvalue E_v , the rotational constant B_v , the centrifugal constant D_v and the turning points R_{\min} and R_{\max} for some excited electronic states of the molecules NaBr and KBr. Also given in Fig. FS3 the potential energy curve of the ground state of NaBr and KBr investigated using ECP10MDF_AV5Z basis set for Br with s, p and d functions with their spectroscopic constants provided in Table TS4. While those investigated using ECP28MWB basis and including 2s and 3s, 2p and 3p orbitals of Na and K are given in Fig. FS4 respectively. Their corresponding spectroscopic constants are provided in Table TS5.

On the other hand, we provided in the supplementary material SM2 the numerical values of the potential energies and dipole moments as function of the internuclear distance.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemphys.2018.09.037>.

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