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Theoretical Electronic Structure of the Lowest-Lying Electronic States of the CaBr Molecule

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Abstract

Sixteen doublet and nine quartet potential energy curves of the low-lying electronic states, in the $^{2s+1}\Lambda^{(\pm)}$ representation of the molecule CaBr, have been investigated via the Multireference Configuration Interaction method (MRCI) and second-order Multireference Perturbation Theory (RPST2). The harmonic vibrational frequency ω_e, the internuclear distance at equilibrium R_e, the rotational constant B_e, the electronic energy with respect to the minimum ground state energy T_e, and the permanent dipole moment at the internuclear distance at equilibrium μ have been calculated. By using the canonical functions approach, the eigenvalues E_v, the rotational constant B_v and the abscissas of the turning points R_{min} and R_{max} have been calculated for the studied electronic states. By comparing the values of the investigated data to the theoretical and experimental results available in the literature shows a good agreement. For the first time 15 new electronic states have been studied theoretically in the present work.

Keywords: *ab initio* calculation, potential energy curves, spectroscopic constants, dipole moment, rovibrational calculation

1. Introduction

In addition to the importance of the alkaline earth monohalides in high-temperature chemistry (D'incan et al., 1991; Verges et al., 1993; Rao et al., 1983; Kaldin et al., 1999) and chemiluminescent reactions (Langhoff et al., 1986; Yang et al., 2004; Handy et al., 1989; Dykstra, 1977) recerent studies have been done for these molecules (Rice et al., 1985; Törring et al., 1989; Harris et al., 1993; Murphy et al., 1990, 1995; Berg et al., 1993). The valence structure of the free Ca^+ ion is perturbed by the negative point charge (Allouche et al., 1993) with a single valence electron around two closed shell ion. The first spectra of CaBr molecule have been observed by Walters and Barratt (1927). The vibrational assignments appearing in Rosen (1980) tables were made by Harrington (1942). Huang et al. (2008) investigated the molecular absorption spectra of CaBr molecule using a high resolution scale spectrometer; and laser-induced fluorescence spectra has been measured by Keijzer et al. (1966). The dissociation energy of this molecule has been determined by Garay Salazar et al. (1997). High-precision Stark effect measurements have been performed on the electronic and vibrational ground state of $Ca^{79}Br$ molecule and the dipole moments are determined by Kindt et al. (1983). Reaction cross-section and product polarization in the $Ca(^1D_2)$ + HBr → CaBr(A, B) + H reaction has been studied by measuring its chemiluminescence by (Garay Salazar et al., 1995). Laser excitation spectroscopy with hyperfine structure of CaBr of $A^2\Pi$-$X^2\Sigma^+$ and $B^2\Sigma^+$ - $X^2\Sigma^+$ systems are made by Bernath et al. (1981).

The lag for theoretical calculation for higher excited electronic states stimulated us to investigate in the present work the Potential Energy Curves (PECs) of the 25 low-lying electronic states with the high level MRCI calculation and multireference perturbation theory methods with large basis sets. The spectroscopic constants T_e, R_e, ω_e and B_e of the molecule CaBr have obtained for the considered electronic states along with the static dipole moment. Based on the electronic structure of the investigated electronic states and by using the canonical functions approach (Kobeissi et al., 1989; Korek et al., 1992, 1999), the energy eigenvalue E_v, the rotational and the the centrifugal distorsion constant B_v, and D_v respectively and the abscissas of the turning points R_{min} and R_{max} have been calculated, for different values of the vibrational constants v, for the studied electronic states.

2. Theoretical Details

We start an *ab initio* study for the CaBr molecule by using a Hartree-Fock calculayion.The assumption behind this technique is that any one electron moves in a potential which is a spherical average of the potential due to all the other electrons and the nucleus. But this technique does not consider the instantaneous coulombic interactions between the electrons. The configuration interaction (CI) is a method used to avoid this deficiency where the awavefunction can be expressed as a linear combination of all possible n-electron singly, doubly, triply … excited electronic states represented by Slater determinants arising from a complete set of spinorbitals. An improvement of the CI method is obtained by the multiconfiguration self-consistent field method (MCSCF) where the CI coefficients are optimized. The complete active-space self-consistent field method (CASSCF) is an efficient development for the excited states in which the spinorbitals are divided into three classes: inactive, active and virtual orbitals. In the present work two methods of calculation have been used i) In the CI methods the wavefunction Φ_0 of the ground state is used as a reference configuration. In multireference configuration interaction (MRCI), a set of reference configurations is created, from which excited determinants are formed for use in a CI calculation ii) The Rayleigh-Schrödinger perturbation theory (RSPT2), it is based on a CASSCF reference wavefunction, which takes in account of all near degeneracy effects in the electronic structure that occurs in many situations. Remaining dynamic effects are added using the perturbative method, which calculates the first order wavefunction and the second order energy using the CASSCF wavefunction as the zeroth-order reference function (Werner & Knowles, 1985; Knowles & Werner, 1985). All calculations were performed with the MOLPRO program package (Molpro) taking advantage of a graphical user interface GABEDIT (Allouch, 2011). Calcium and Bromine atoms are treated through a pseudo potential approach. From Molpro library the basis set are chosen for s, p and d functions using respectively ECP10MWB and ECP28MWB for Ca and Br atoms. Through the MCSCF/MRCI-RSPT2 calculations, the wave function is studied under C_{2v} symmetry. The $1s^2\ 2s^2\ 2p^6$ of Ca and $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ of Br atoms were frozen in the MCSCF procedure. The number of closed-shell orbitals is 7 (3σ, $2\pi_x$, $2\pi_y$, 0δ) and the number of active orbitals is 14.

3. Results and Discussion

The potential energy curves of CaBr molecule have been obtained using the MRCI and RSPT2 computational methods. The potential energy curves of CaBr molecule have been calculated for a wide internuclear distance range 1.5 Å < R< 11.5 Å. The potential energy curves for 25 electronic states in the representation $^{2s+1}\Lambda^{(+/-)}$ calculated via MRCI method are drawn in Figures 1–3 for the $^{2,4}\Sigma^{(+/-)}$, $^{2,4}\Pi$, $^{2,4}\Delta$ and $^{2}\Phi$ states. The number of investigated electronic states is limited to 25 because of undulation starts to appears with higher electronics states. The origin of these undulations is unrelated to avoided crossing between adiabatic electronic states; maybe it is directly attributed to the atomic orbital oscillations of the atoms when approaches each other with varying electron density.

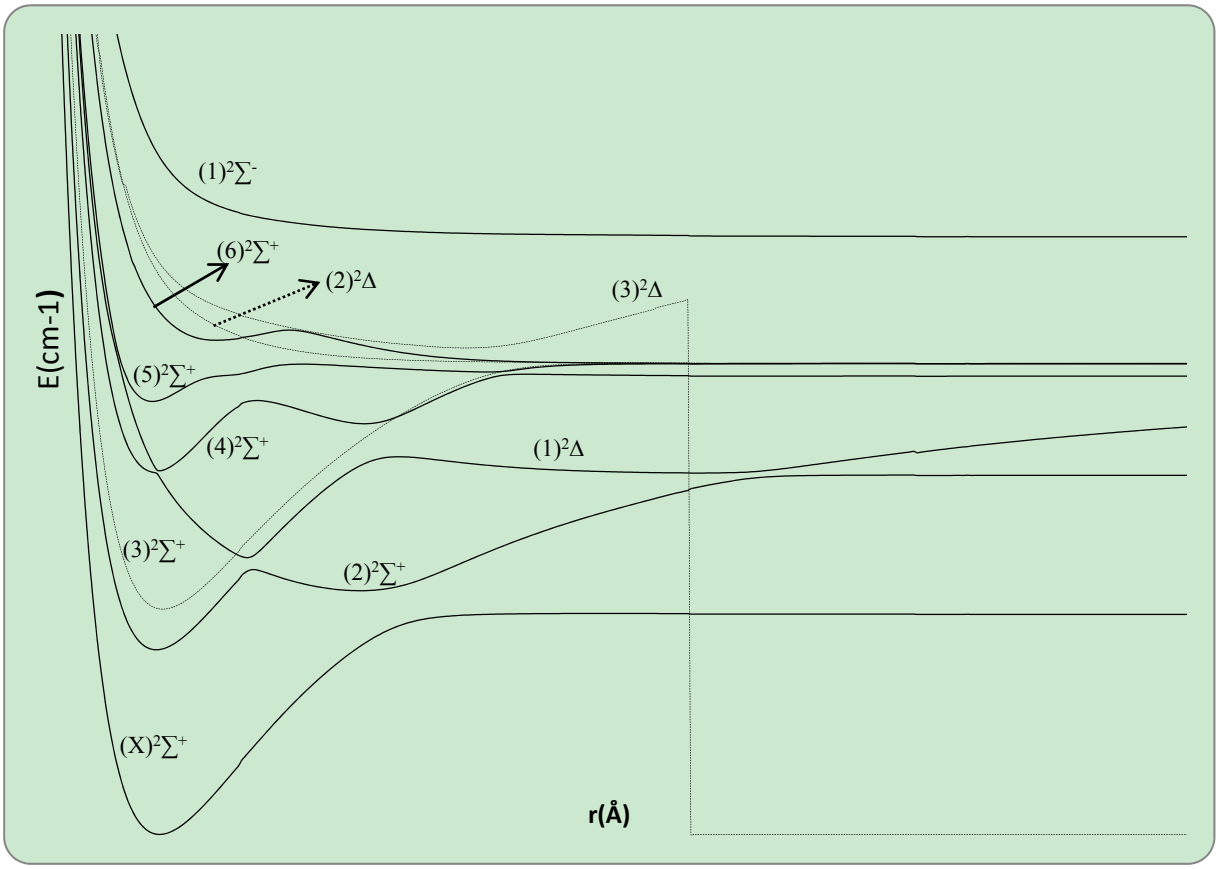

Figure 1. Potential energy curves, calculated by MRCI method, for the $^2\Sigma^{\pm}$ and $^2\Delta$ states of the molecule CaBr

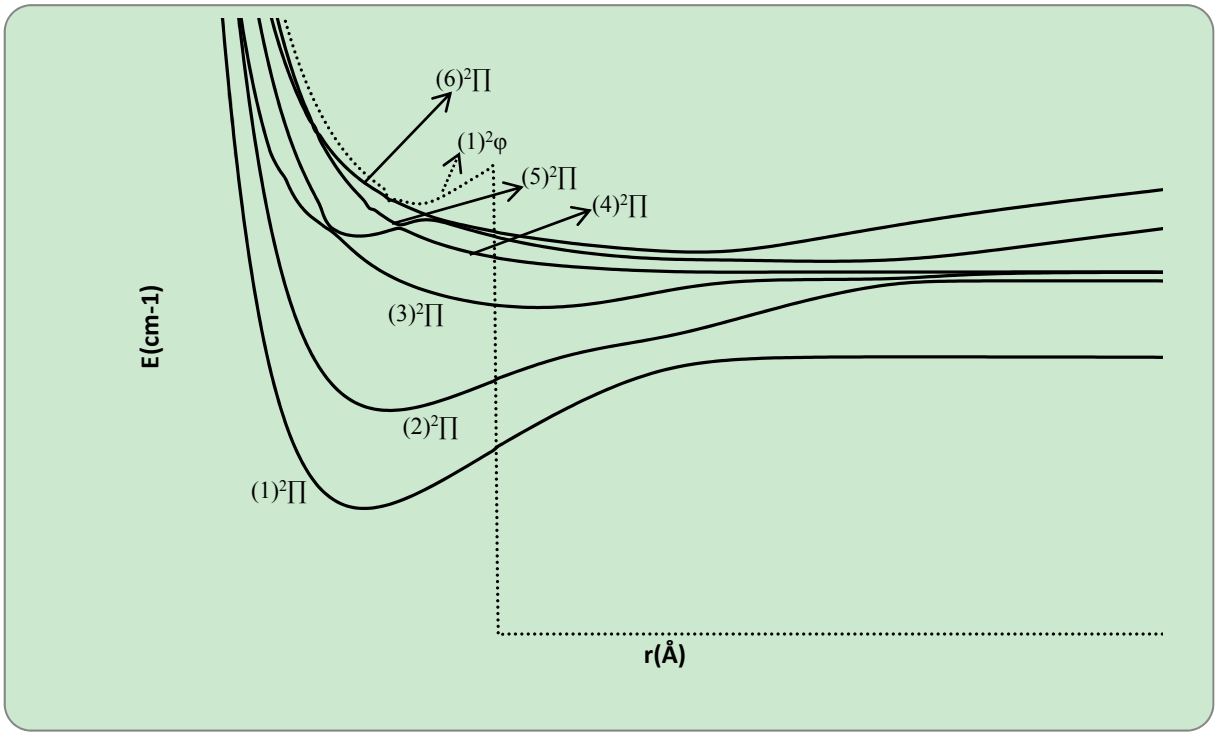

Figure 2. Potential energy curves, calculated by MRCI method, for the $^2\Pi$ and $^2\Phi$ states of the molecule CaBr

Because of the shallow PECs of the quartet electronic states around the equilibrium positions R_e, the forces that bind the two atoms are very weak and the dissociation energies are very low.

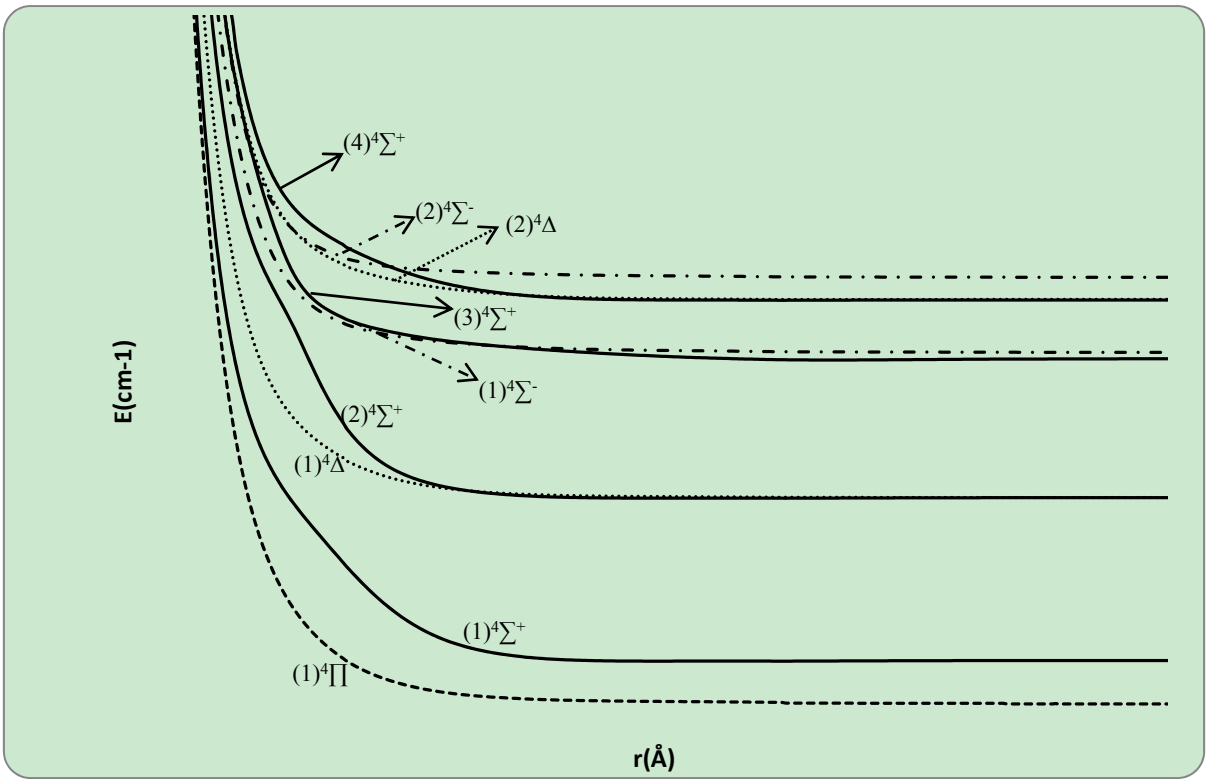

Figure 3. Potential energy curves, calculated by MRCI method, for the $^4\Sigma^{\pm}$, $^4\Delta$, and $^4\Pi$ states of the molecule CaBr

Two states of different symmetry cross each other; their wavefunctions remain unperturbed and are adiabatic solutions of the Schrödinger equation. If they have the same symmetry, the two states will only be diabatic solutions of the problem. They will mix with each other to give two adiabatic solutions where the crossing becomes avoided. In fact, the avoided crossing regions are likely to be a leakage channels along which the molecules flow from the higher down to the lower potential energy curves. Such crossings or avoided crossings can dramatically alter the stability of molecules. If these crossings are overlooked then low barrier transitions can be missed and an incorrect chemical picture will arise. In the present work one can notice that, the crossing and avoided crossing are at low and higher doublet excited electronic states, while they are only at higher quartet electronic states. The positions of these crossings and avoided crossing along with the energy difference at the avoided crossing are given in Table 1.

Table 1. Positions of the crossing and avoided crossings between the different electronic states of the molecule CaBr

State1	State2	crossing r_c(Å)	Avoided crossing r_{av}(Å)	ΔE_{av}(cm^{-1})
$(X)^2\Sigma^+$	$(2)^2\Sigma^+$		5.08	2273.7
$(2)^2\Sigma^+$	$(3)^2\Sigma^+$		3.58 and 8.50	1291.8 and 1608
$(3)^2\Sigma^+$	$(4)^2\Sigma^+$		2.71	360.1
$(1)^2\Delta$	$(3)^2\Sigma^+$	3.44		
$(1)^2\Delta$	$(4)^2\Sigma^+$	4.97		

$(2)^2\Delta$	$(6)^2\Sigma^+$	3.49		
$(3)^2\Pi$	$(4)^2\Pi$		2.47	510.2
$(4)^2\Pi$	$(5)^2\Pi$		2.89	453.5
$(5)^2\Pi$	$(6)^2\Pi$		3.16	24.5
$(6)^2\Pi$	$(1)^2\varphi$	2.82 and 2.84		
$(2)^4\Sigma^+$	$(1)^4\Delta$	4.69		
$(3)^4\Sigma^+$	$(1)^4\Sigma^-$	4.90		
$(4)^4\Sigma^+$	$(2)^4\Delta$	5.20		
$(4)^4\Sigma^+$	$(2)^4\Sigma^-$	3.91		

By fitting the PECs, calculated by MRCI and RSPT2 methods, around the minimum to a polynomial in R, one can obtain the transition energy with respect to the energy minimum for the ground state T_e, the internuclear distance at equilibrium R_e, the harmonic frequency ω_e and the rotational constants B_e. These values along with the available data, either theoretical or experimental, in literature are given in Table 2. One can notice the absence of these constants for some potential energy curves because of the crossing or avoid crossing near the minima of these curves. The positions of the maxima and the spectroscopic constants of the double well potential energy curves of the $(2, 4, 5, 6)^2\Sigma^+$ states are also given in Table 2.

In literature there are fragmented data on the molecule CaBr; for T_e there are experimental values (Keijzer et al., 1996; Bernath et al., 1981; Oudejans et al., 1999) for 3 excited electronic states and theoretical results for 4 excited electronic states (Törring et al., 1989; Allouche et al., 1993). The comparison of our calculated values of T_e, by using the MRCI and RSPT2 techniques, with the experimental data in literature (Keijzer et al., 1996; Bernath et al., 1981; Oudejans et al., 1999) shows that: i) a better precision is obtained by using MRCI method than the RSPT2, ii) a very good agreement for the state $(1)^2\Pi$ by using the 2 techniques. By comparison with another alkaline earth monofluoride (CaF molecule) we can notice that, the deviation from experiment is smallest for (1) $^2\Pi$ ($\Delta T_e/T_e \approx 2.7\%$) and larger for (2) $^2\Pi$ ($\Delta T_e/T_e = 14.5\%$ and 17.9). This deviation may be explained by the amount of d orbital participation in the different states (Bündgen et al., 1991); this problem is well known in such types of molecules (Partridge et al., 1983; Pettersson et al., 1983) which may be explained by the D orbital of the alkaline earth atom. The choice of the basis set is a tedious work, but even with the large basis the discrepancy remained large with higher states (Partridge et al., 1983). The comparison of our results with the theoretical data available in literature (Allouche et al., 1993) is not informative since it shows a relative difference $0.7\% \leq \Delta T_e/T_e \leq 40.7\%$ which is depending on the different techniques used in these calculations.

Table 2. Spectroscopic constants for the ground and low-lying excited $^2\Lambda^{(+)}$ states of CaBr molecule

		$(1)^2\Sigma^+$			$(1)^2\Pi$			$(2)^2\Sigma^+$		
			ΔX/X (CI) %	ΔX/X (RS2) %		ΔX/X (CI) %	ΔX/X (RS2) %		ΔX/X (CI) %	ΔX/X (RS2) %
T_e (cm^{-1})	MRCI	0			16383.4			18465.3		
	RS2	0			16411.6			19074.1		
	Exp[a]	0			15958.5	2.6	2.8	16383.1	12.7	16.4
	Exp[b]	0			15958.4	2.6	2.8	16383.1	12.7	16.4
	Exp[c]	0			15950	2.7	2.8	16380	12.7	16.4
	Theo[d]	0			15120	8.3	8.5	16210	13.9	17.6
	Theo[e]	0			17367	5.6	5.5	18602	0.7	2.5
	Theo[e]	0			17263	5.0	4.9	18722	1.3	1.8

	Theo[e]	0			16670	1.7	1.5	18263	1.1	4.4
	Theo[e]	0			17820	8.0	7.9	21024	12.1	10.2
	Theo[e]	0			15120	8.3	8.5	16210	13.9	17.6
	Max							max		
	MRCI							24367.9		
	RS2							22517		
R_e (Å)	MRCI	2.697			2.669			2.667		
	RS2	2.661			2.672			2.685		
	Exp[b]	2.5935	3.9	2.6	2.576	3.6	3.7	2.567	3.8	4.5
	Theo[d]	2.594	3.9	2.5						
	Max							max		
	MRCI							4.622		
	RS2							4.419		
	MRCI							2.667		
ω_e cm^{-1}	MRCI	300.32			295.18					
	RS2	276.01			282.02					
	Exp[a]	285.73	5.1	3.4	288.33	2.3				
	Exp[b]	285.73	5.1	3.4	288.56	2.2				
	Max									
	MRCI									
	RS2									
Be cm^{-1}	MRCI	0.0871			0.0886			0.0887		
	RS2	0.0862			0.0884			0.0876		
	Exp[a]	0.0944	7.7	8.6	0.0957	7.4	7.6	0.0965	8.0	9.2
	Exp[b]	0.0944	7.7	8.6	0.0957	7.4	7.6	0.0965	8.0	9.2
	Max							max		
	MRCI							0.0295		
	RS2							0.0323		
		$(1)^2\Delta$			$(2)^2\Pi$					
			ΔX/X (CI) %	ΔX/X (RS2) %		ΔX/X (CI) %	ΔX/X (RS2) %			
T_e cm^{-1}	MRCI	22526.6			29126.7					
	RS2	22945.2			30007.3					
	Exp[a]	-------			-------					
	Exp[b]	-------			-------					
	Exp[c]	-------			25430	14.5	17.9			
	Theo[d]	16300	38.2	40.7	27400	6.2	9.5			
	Theo[e]	18520	21.6	23.8	28289	2.9	6.0			
	Theo[e]	22310	0.9	2.8	28804	1.1	4.1			
	Theo[e]	16300	38.2	40.7	33556	13.2	10.5			

	Theo[e]		32256	9.7	6.9
	Theo[e]		27400	6.2	9.5
R_e	MRCI	2.735	2.832		
(Å)	RS2	2.748	2.864		
ω_e	MRCI	237.60	218.54		
cm^{-1}	RS2	231.27	205.47		
B_e	MRCI	0.0844	0.0787		
cm^{-1}	RS2	0.0835	0.0769		

Table 2. Continue

		$(5)^2\Sigma^+$	$(3)^2\Pi$	$(6)^2\Sigma^+$	$(3)^2\Delta$	$(6)^2\Pi$	$(1)^2\varphi$
T_e (cm^{-1})	MRCI	43296.32	42512.48	49420.02	48793.97	49718.28	56016.68
	RS2	44551.25	41126.46	48466.63	47359.55	48631.84	54691.42
	max	**max**					
	MRCI	46244.58					
	RS2	43890.44					
R_e (Å)	MRCI	2.636	3.732	3.245	5.525	4.704	2.993
	RS2	2.707	3.598	3.024	5.006	4.393	3.264
	max	**max**					
	MRCI	5.869					
ω_e (cm^{-1})	MRCI	250.19	63.077	110.82	53.910	90.355	454.56
	RS2	165.61	100.894	156.84	61.691	89.793	394.18
	max	**max**					
	MRCI	47.827					
	RS2	195.159					
B_e (cm^{-1})	MRCI	0.0908	0.0446	0.0599	0.0206	0.0285	0.0705
	RS2	0.0860	0.0487	0.0690	0.0251	0.0327	0.0592
	max	max					

[a]Keijzer et al., 1996, [b]Bernath et al., 1989, [c]Oudejans et al., 1999, [d]Törring et al., 1989, [e]Allouche et al., 1993.

By comparing our calculated values of R_e, ω_e, and B_e, for the ground and the 2 states (1) $^2\Pi$ and (2) $^2\Sigma^+$, with the experimental (Keijzer et al., 1996; Bernath et al., 1981) and the theoretical values (Törring et al., 1989) in literature one can find a good agreement with a relative difference varies between 1.9% and 11.6% either calculated by MRCI or RSPT2 techniques. The comparison of our calculated spectroscopic constants for the other investigated electronic states with other values in literature is not possible because they are given here for the first time.

4. Vibration-Rotation Calculation

A promising approach for realizing a quantum computer is based on using the vibrational states of molecules to represent qubits and tailored femtosecond laser pulses to implement quantum gate operations (Tesch et al., 2001; Mishima et al., 2008). This vibrational state approach has several advantages: i) the number of qubits is proportional to the number of vibrational degrees of freedom, ii) more qubits can be realized using a N-atom molecule, iii) the vibrational states of molecules are stable over the time scales of interest, iv) the number of qubits is not limited to ten and, v) by using more vibrational states, it may be possible to represent quantum information units having more than two states |0>, |1>, |2>, |3>…. (Zhao & Babikov, 2006). Using the the canonical functions approach (Kobeissi et al., 1989; Korek et al., 1992, 1999) the radial Schrödinger equation

can be replaced by the system of equations

$$\phi_0''(r) + [e_0 - U(r)]\phi_0(r) = 0 \tag{1}$$

$$\phi_1''(r) + [e_0 - U(r)]\phi_1(r) = -[e_1 - R(r)]\phi_0(r) \tag{2-1}$$

$$\phi_2''(r) + [e_0 - U(r)]\phi_2(r) = -[e_1 - R(r)]\phi_1(r) - e_2\,\phi_0(r) \tag{2-2}$$

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The comparison of our calculated values of B_v and D_v for the states $X^2\Sigma^+$ and $(1)^2\Pi$ with the available experimental values in literature, measured by (Bernath et al., 1981), shows a very good agreement with relative differences $\delta B_v/B_v$ equal to 8.4% for $X^2\Sigma^+$ and 7.7% for $(1)^2\Pi$ states and $0.9\% \leq \delta D_v/D_v \leq 3.4\%$ for these 2 states. These constants have not been calculated for other electronic states because of the breakdown of the Born-Openheimer approximation at the crossing and avoided crossing of the investigated potential energy curves.

5. Dipole Moment

The permanent electric dipole moment μ should be amongst the most reliably predicted physical properties because its expectation value is sensitive to the nature of the least energetic and most chemically relevant valence electrons. Among the utility of the permanent electric dipole moment μ, it enters into the description of light-matter interaction in resonant spectroscopy, the relative intensity predictions of pure rotational transitions and in the orientating molecules. The degree of alignment depends on the magnitude of μ. This approach has been used to study the angular distributions in photodissociations (Oudejans et al., 1999) and collision processes (Loesch, 1995). By taking the Ca atom as an origin in our calculation, the permanent dipole moments of the investigated electronic states have been investigated for the 25 lowest doublet and quartet electronic states of the molecule CaBr. The calculated values of the dipole moments (in Debye) for these electronic states in terms of the internuclear distance R are plotted in Figures 4–6.

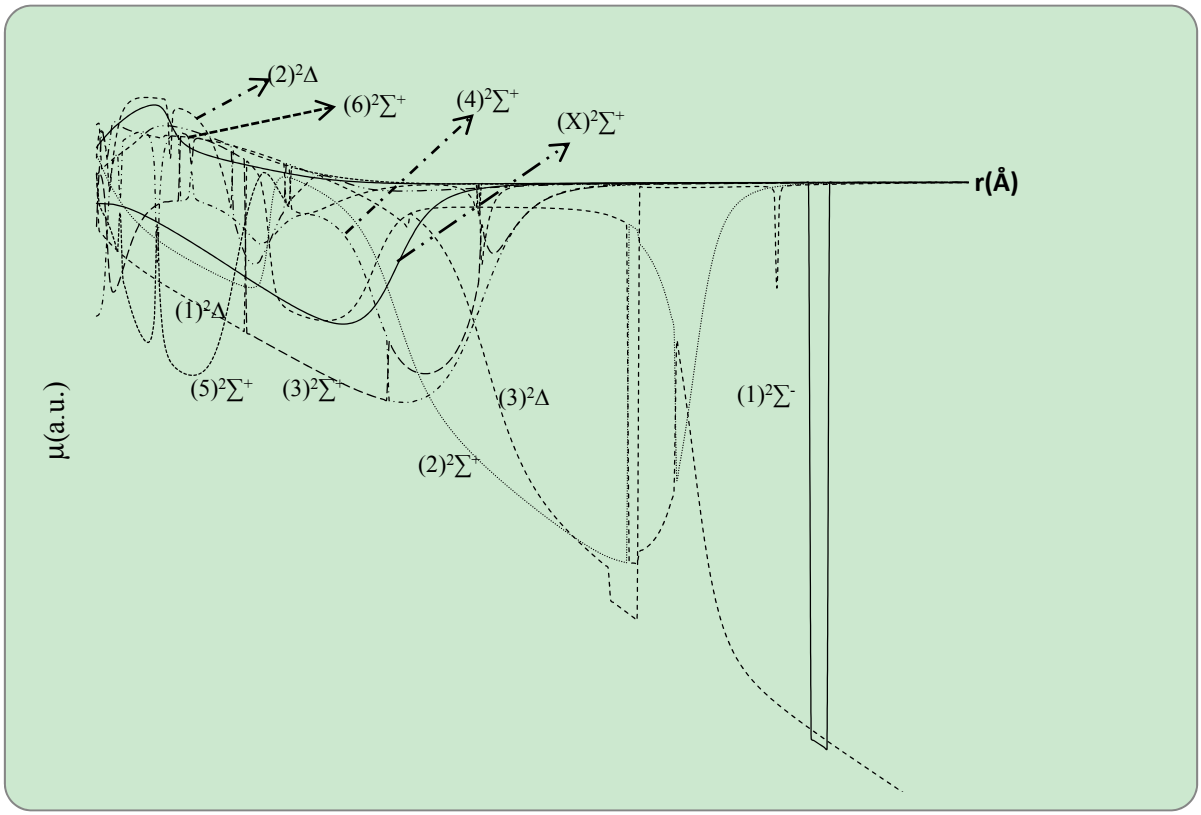

Figure 4. Permanent dipole moment, calculated by MRCI method, for the $^2\Sigma^{\pm}$ and $^2\Delta$ states of the molecule CaBr

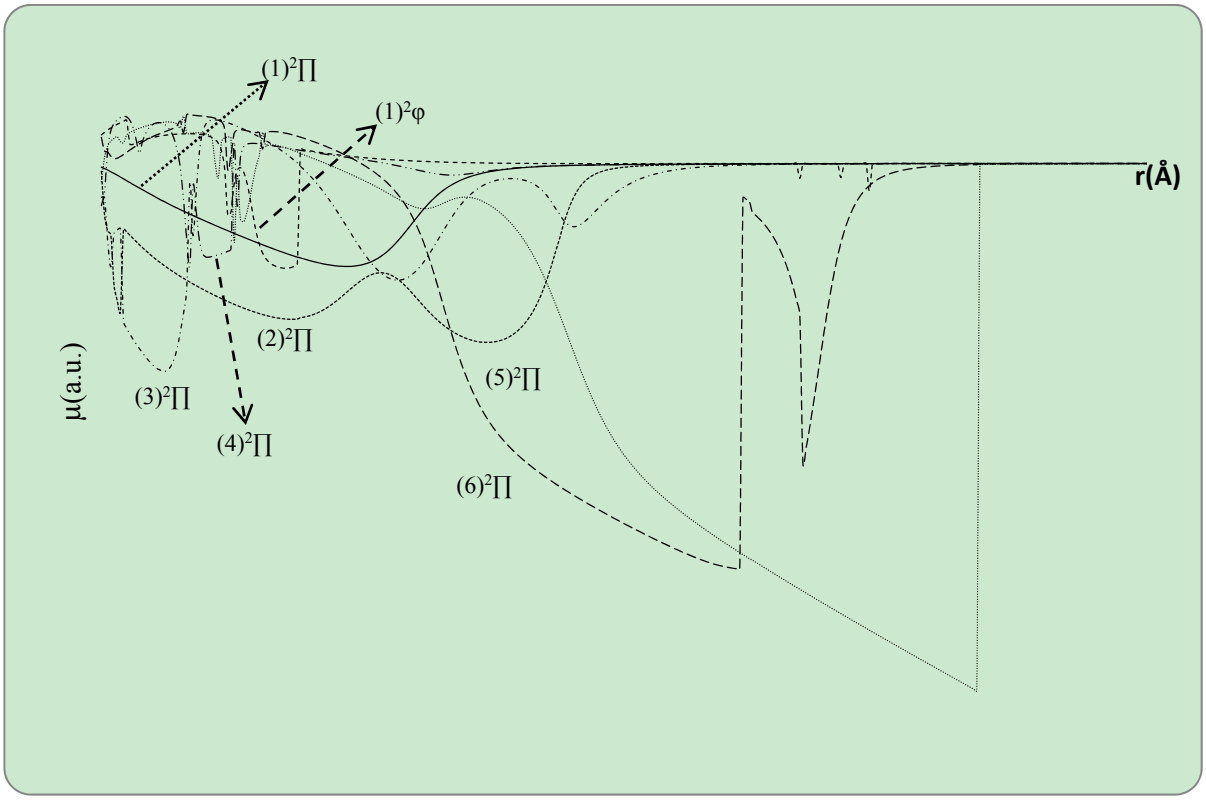

Figure 5. Permanent dipole moment, calculated by MRCI method, for the $^2\Pi$ and $^2\Phi$ states of the molecule CaBr

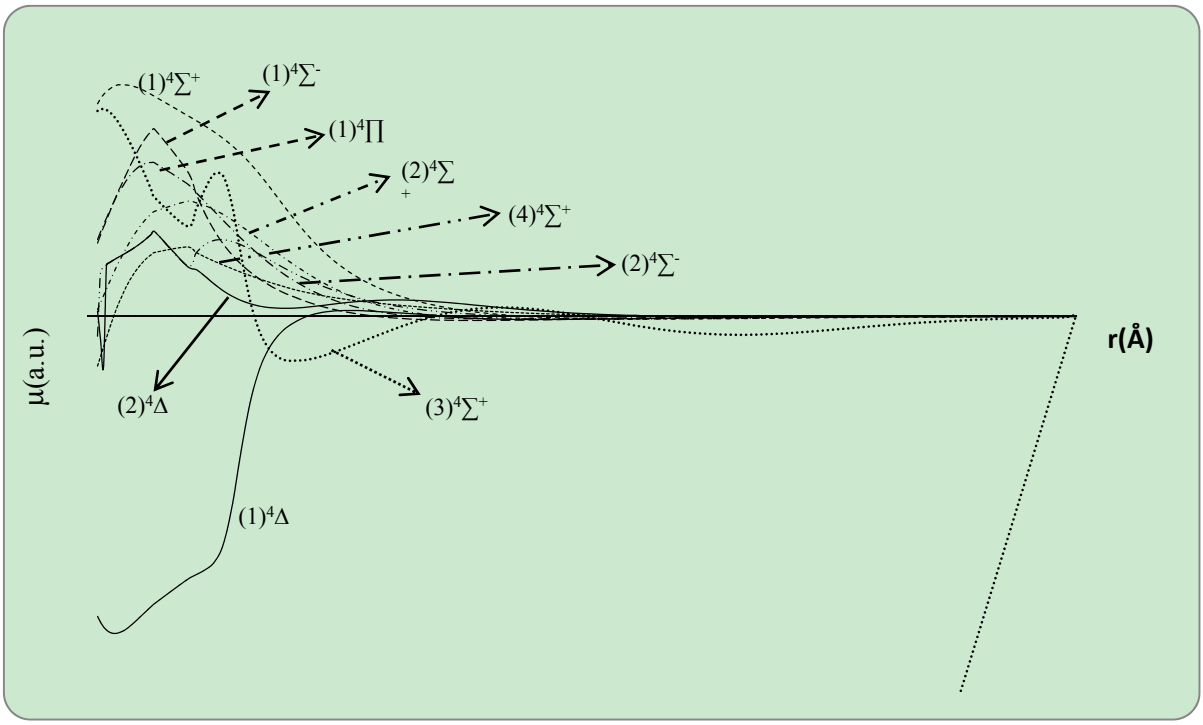

Figure 6. Permanent dipole moment, calculated by MRCI method, for the $^4\Sigma^{\pm}$, $^4\Delta$, and $^4\Pi$ states of the molecule CaBr

We notice that these curves tend to zero when R tends to infinity. All these calculations have been performed by using the MOLPRO program. One can notice the agreement between the position of the avoided crossing of the PECs and the crossings of dipole moment curves of these states which can be considered as confirmation of the accuracy of the present work.

6. Conclusions

In the present work, an *ab initio* calculation has been performed for the 25 low lying doublet and quartet electronic states of CaBr molecule using the Multireference Configuration Interaction method (MRCI) and second-order Multireference Perturbation Theory (RSPT2) for the ground and low-lying excited states. These calculations were preceded by Multi-configurational self-consistent field (MCSCF) calculations (Werner & Knowles, 1985; Knowles & Werner, 1985, Atkins & Friedman, 2005 (chapter 7, 8, 9)) in which all valence molecular orbitals were optimized. From Molpro library the basis set are chosen for s, p and d functions using respectively ECP10MWB and ECP28MWB for Ca and Br atoms. The potential energy and the dipole moments curves have been determined along with the spectroscopic constants R_e, B_e, and ω_e for these states. By using the canonical functions approach the eignvalue E_v is calculated from the pure vibrational Equation (1). The rotation constants B_v, the centrifugal distortion constant D_v and the abscissas of the turning points R_{min} and R_{max} have been determined for different electronic states of the molecule CaBr up to the vibrational level v=10 by using Equations (2-n). The comparison of these calculated values with the theoretical and experimental data available in the literature demonstrated a very good accuracy. The present calculated values of T_e are in good agreement with those of the lower experimental electronic states and they are larger by comparing with the higher electronic state $(2)^2\Pi$. The accuracy of our results of T_e with respect to the theoretical values in literature depends on the theoretical technique of calculation**.** We believe that the investigation of new valid excited electronic states for both the ground and low-lying excited electronic states based on *ab initio* calculations can be useful for more investigations of the CaBr molecule and may lead to the investigation of new experimental works. Fifteen new electronic states have been investigated in the present work for the first time

Acknowledgements

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