

# Theoretical Electronic Structure of the Lowest-Lying Electronic States of the CaCl Molecule

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## Abstract

The potential energy curves of 10 doublet and 5 quartet low-lying electronic states of CaCl molecule have been investigated by using the Complete Active Space Self Consistent Field (CASSCF) with Multi Reference Configuration Interaction (MRCI) using effective core potential for both atoms. Based on the investigated PECs, the harmonic frequency  $\omega_e$ , the internuclear distance  $R_e$ , the dipole moment, and the electronic energy with respect to the ground state  $T_e$  have been calculated for the considered electronic states. A rovibrational study has been performed with the calculation of the eigenvalue  $E_v$ , the rotational constant  $B_v$  and the abscissas of the turning points  $R_{\min}$  and  $R_{\max}$ . The comparison between the values of the present work and those available in the literature for several electronic states shows a very good agreement. Nine new excited electronic states have been investigated here for the first time.

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

## 1. Introduction

Alkaline earth monohalides have received, in recent years, considerable attention in addition to their importance in high-temperature chemistry (D'incan et al., 1991; Verges et al., 1993; Kaledin et al., 1999; Childs et al., 1984) and chemiluminescent reactions (Amiot et al 1991; Langhoff et al., 1986; Menzinger et al 1974; Yang et al., 2004; Handy et al., 1989; Dykstra, 1977). Accurate experimental and theoretical data have become available for these monohalides (Ernst et al 1984; Harris et al., 1993; Murphy et al., 1990, 1995; Berg et al., 1993; Bündgen et al 1991). The spectroscopic constants of the  $B^2\Sigma^+-X^2\Sigma^+$  systems are obtained for the first time by using high resolution laser excitation spectroscopy by (Domaille et al., 1977). A rotational analysis of the  $E^2\Sigma^+-X^2\Sigma^+$  transition of CaCl is made by (Berg et al., 1978). Experimental potential energy curves have been constructed for the first time for  $(X)^2\Sigma^+$  and  $(C)^2\Pi$  electronic states of CaCl molecule by (Rao et al., 1983). Energies and electric dipole moments of the low lying electronic states of the alkaline earth monohalides, by applying an electrostatic polarization model, are investigated by (Torrington et al., 1989). Transition energies and permanent and transition dipole moments, of the low-lying states of calcium monohalides, have been evaluated by (Allouche et al., 1993) using the ligand-field approach, proposed by (Rice et al., 1985).

We investigate in the present work the Potential Energy Curves (PECs) for the 15 low-lying electronic states with the high level MRCI calculation. The spectroscopic constants  $T_e$ ,  $R_e$ ,  $\omega_e$  and  $B_e$  of the molecule CaCl have been obtained for the investigated doublet electronic states along with the static dipole moment, the eigenvalue  $E_v$ , the rotational constant  $B_v$ , and the abscissas of the turning points  $R_{\min}$  and  $R_{\max}$ .

## 2. Method

An *ab initio* calculations were performed for CaCl molecule using the multireference configuration interaction method (MRCI) for the ground and low-lying doublet and quartet electronic states. These calculations were preceded by Multi-configuration self-consistent field (MCSCF) calculations (Werner & Knowles, 1985; Knowles & Werner, 1985) in which all valence molecular orbitals were optimized. All calculations were performed with the MOLPRO program package (Molpro) taking advantage of the graphical user interface GABEDIT (Allouch, 2011). Calcium and Chlorine atoms are treated through pseudo potentials approach. Effective Core

Potential-MWB basis set are chosen for both atoms from library of the MOLPRO software. Through the MCSCF/MRCI calculations, the wave function is under  $C_{2v}$  symmetry. The  $1s^2 2s^2 2p^6$  of both atoms were frozen in the MCSCF procedure. The number of closed-shell orbitals is 7 ( $3\sigma, 2\pi_x, 2\pi_y, 0\delta$ ) and the number of active orbitals is 5. The energies of PECs are calculated in the range of internuclear distances  $1.5 \leq R \leq 11.5 \text{ \AA}$ .

### 3. Results

The calculations for the doublet and quartet PECs, for the lowest 15 electronic states of the CaCl molecule, have been performed for the internuclear range  $1.5 \text{ \AA} \leq R \leq 11.5 \text{ \AA}$  in the representation  $^{2s+1}\Lambda^{(+/-)}$  (Figures 1-3).

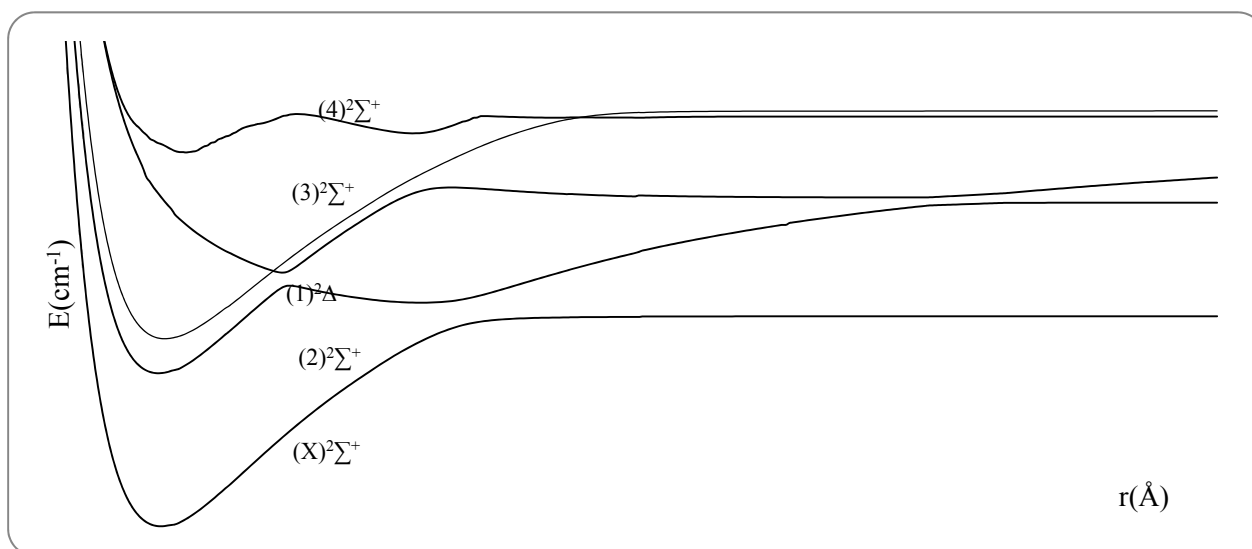


Figure 1. Potential energy curves for the  $^2\Sigma^+$ ,  $^2\Delta$  and  $^2\Sigma^-$  states of the molecule CaCl

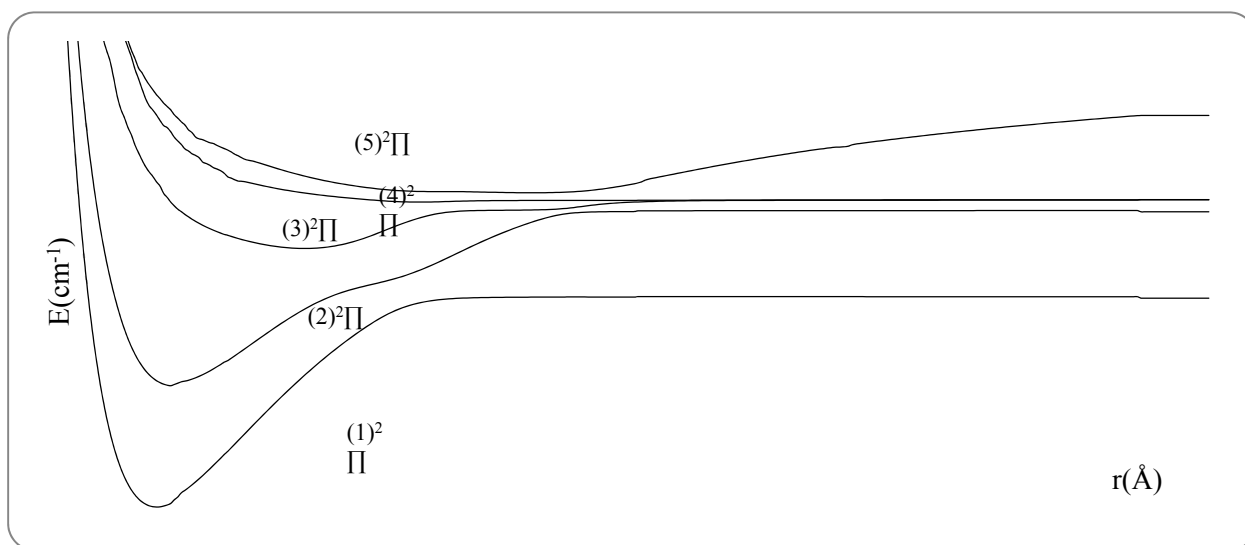


Figure 2. Potential energy curves for the  $^2\Pi$  states of the molecule CaCl

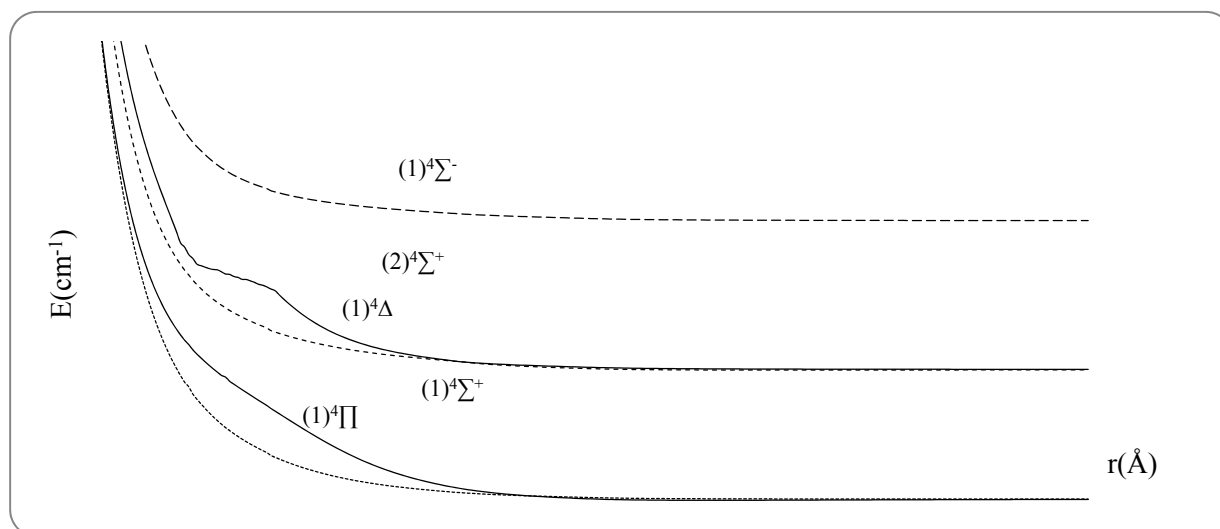


Figure 3. Potential energy curves for the  $^4\Sigma^+$ ,  $^4\Delta$ ,  $^4\Pi$  and  $^4\Sigma^-$  states of the molecule CaCl

The PECs of the low-lying electronic states intercross each other in several places which are displayed in Table 1 for all the considered electronic states.

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

State1	State2	crossing	Avoided crossing	
		$r_c(\text{\AA})$	$r_{av}(\text{\AA})$	$\Delta E_{av}(\text{cm}^{-1})$
$(1)^2\Sigma^+$	$(2)^2\Sigma^+$		5.11	3161.8
			3.58	1718.7
$(2)^2\Sigma^+$	$(3)^2\Sigma^+$		and	and
			8.95	1006.8
$(1)^2\Delta$	$(3)^2\Sigma^+$	3.47		
$(1)^2\Delta$	$(4)^2\Sigma^+$	6.03		
$(1)^2\Pi$	$(2)^2\Pi$		4.60	3588.3
$(2)^2\Pi$	$(3)^2\Pi$		5.98	601.7
$(1)^4\Sigma^+$	$(1)^4\Pi$	5.07		

In order to calculate the spectroscopic constants: transition energy with respect to the energy minimum for the ground state  $T_e$ , equilibrium internuclear distance  $R_e$ , harmonic frequency  $\omega_e$  and the rotational constants  $B_e$ , the calculated potential energy values were fitted to a polynomial in  $R$  around the minimum. These values along with the experimental and theoretical data available in literature are displayed in Table 2. Our MRCI computational equilibrium position is in good agreement compared with the experimental value of (Allouche et al., 1993) with a discrepant relative difference  $\delta R_e/R_e=3.7\%$  for  $(X)^2\Sigma^+$  state. The comparison of the harmonic frequency  $\omega_e$ , calculated in the present work for the ground state, is in acceptable agreement by comparing to those given by (Domaille et al., 1977; Berg et al., 1978) with the relative differences 8.6% and 8.9% respectively. Similar results are obtained by comparing our calculated value of  $B_e$  to those given in literature (Domaille et al., 1977; Berg et al., 1978) where the relative differences are 7.8% for  $(X)^2\Sigma^+$  state and 7.7% for  $(2)^2\Sigma^+$  state.

Table 2. Spectroscopic parameters  $T_e(\text{cm}^{-1})$ ,  $R_e(\text{\AA})$ ,  $\omega_e(\text{cm}^{-1})$  and  $B_e(\text{cm}^{-1})$  for the ground and low-lying excited  $^2\Lambda^{(+)}$  states of CaCl molecule

		$(1)^2\Sigma^+$		$(1)^2\Pi$		$(2)^2\Sigma^+$		$(1)^2\Delta$		$(2)^2\Pi$		$(3)^2\Pi$	$(5)^2\Pi$	
			$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$			
$T_e$	MRCI	0		16588.7		18944.7		23216.3		30476.6		46250.8	52647.3	
	Exp[a]	0		-----		16856.6	12.3%	-----		-----				
	Exp[b]	0		-----		-----		-----		-----				
	Exp[c]	0		-----		-----		14800	56.8%	-----				
	Theo[d]	0		16130	2.8%	16850	12.4%	-----		-----				
					17644	5.9%	19253	1.6%	19319	20.1%	26540	14.8%		
					17484	5.1%	19317	1.9%	22960	1.1%	29051	4.9%		
					16986	2.3%	18932	~0.0%	16040	44.7%	29626	2.8%		
					17884	7.2%	21408	11.5%			34407	11.4%		
					15630	6.1%	17210	10.0%			32612	6.5%		
				16365	1.3%	18616	1.7%			27000	12.8%			
	<b>max</b>					<b>max</b>								
	MRCI					27681.9								
$R_e$	MRCI	2.528		2.501		2.507		2.563		2.655		3.751	5.668	
	Theo[d]	2.437	3.7%											
		<b>max</b>				<b>max</b>								
	MRCI					4.70								
$\omega_e$	MRCI	337.86		330.02		333.9		302.83		263.56		124.40	45.28	
	Exp[a]	369.80	8.6%			366.8	8.9%							
	Exp[b]	370.21	8.9%											
		<b>max</b>				<b>max</b>								
	MRCI					887.65								
$B_e$	MRCI	0.140		0.143		0.142		0.136		0.127		0.063	0.027	
	Exp[a]	0.152	7.8%			0.154	7.7%							
	Exp[b]	0.152	7.8%											
		<b>max</b>				<b>max</b>								
	MRCI					0.040								

<sup>(a)</sup>Domaille et al., 1977, <sup>(b)</sup>Berg et al., 1978, <sup>(c)</sup>Klynning et al., 1981, <sup>(d)</sup>Allouche, et al., 1993.

The comparison of our calculated values of  $T_e$  for the different investigated electronic states with the available experimental data in literature (Rice et al., 1985; Domaille et al., 1977; Huber et al., 1978) shows a very good agreement for the first excited states  $(1)^2\Pi$  with relative difference  $\delta T_e/T_e=2.8\%$  and this agreement becomes larger for the 2 excited electronic states  $(2)^2\Sigma^+$  and  $(2)^2\Pi$  with the relative differences 12.4% and 14.8% respectively. The discrepancy between our calculated values of  $T_e$  with the theoretical calculated values of the literature (Allouche et al., 1993) depends on the technique of calculation of these values; while the relative difference is  $0.0\% \leq \delta T_e/T_e \leq 6.5\%$  using some techniques (Rice et al., 1985; Torring et al., 1989, with or without

polarization) for the electronic states  $(1)^2\Pi$ ,  $(2)^2\Sigma^+$  and  $(2)^2\Pi$  this relative difference becomes  $7.2\% \leq \delta T_e/T_e \leq 44.7\%$  for other techniques (Rice et al., 1985; Topping et al., 1989, with or without polarization) of calculation (Allouche, et al., 1993). One can notice that, by using one technique of calculation (Rice et al., 1985; Topping et al., 1989) there is a very good agreement with our results for the state  $(2)^2\Sigma^+$  where the relative difference is  $\delta T_e/T_e=0.0\%$  while this agreement deteriorate by using the same technique of calculation for the state  $(1)^2\Delta$  where relative difference is  $\delta T_e/T_e=44.7\%$ . The largest relative difference for this state is 56.8% which is corresponding to the value obtained by (Klyning et al., 1981).

By using the canonical functions approach (Kobeissi et al., 1989; Korek et al., 1992; Korek et al., 1999), the eigenvalue  $E_v$ , the rotational constant  $B_v$ , the centrifugal distortion constant  $D_v$ , and the abscissas of the turning point  $R_{\min}$  and  $R_{\max}$  have been calculated for the investigated electronic states. Table 3 displays these results for the ground state up to  $v=101$  as a sample (the data for the other states are available with authors). The comparison of our calculated values of  $E_v$ ,  $R_{\min}$  and  $R_{\max}$  to those obtained by (Rao et al., 1983) for the two states  $(X)^2\Sigma^+$  and  $(2)^2\Pi$ , shows that our calculated values for  $E_v$  are systematically larger with an average relative difference of 14.5% while our calculated values for  $R_{\min}$  and  $R_{\max}$  are in good agreement with an average relative difference 4.3%.

Table 3. Values of the eigenvalue  $E_v$ , the rotational constant  $B_v$ , the centrifugal distortion constants  $D_v$  (in  $\text{cm}^{-1}$ ) and the abscissas of the turning points (in  $\text{\AA}$ ) of the  $(X)^2\Sigma^+$  state of CaCl molecule up to  $v=10$

v	$E_v(\text{cm}^{-1})$	$R_{\min}(\text{\AA})$		$R_{\max}(\text{\AA})$		$B_v \times 10^2 (\text{cm}^{-1})$	$D_v \times 10^8 (\text{cm}^{-1})$	
		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$				$\left[\frac{\Delta X}{X}\right]$
0	157.29		2.461		2.612	13.9	12.02	
	183.43 <sup>a</sup>	14.2%	2.371 <sup>b</sup>	3.7%	2.511 <sup>b</sup>			4.0%
			2.338 <sup>c</sup>	5.2%	2.503 <sup>c</sup>			4.3%
1	453.10		2.416		2.683	13.724	10.053	
	548.34 <sup>a</sup>	17.3%	2.325 <sup>b</sup>	3.9%	2.569 <sup>b</sup>			4.4%
			2.311 <sup>c</sup>	4.5%	2.553 <sup>c</sup>			5.0%
2	759.88		2.386		2.723	13.769	7.779	
	910.63 <sup>a</sup>	16.5%	2.296 <sup>b</sup>	3.9%	2.612 <sup>b</sup>			4.2%
			2.290 <sup>c</sup>	4.1%	2.589 <sup>c</sup>			5.1%
3	1082.81		2.360		2.760	13.685	11.878	
	1270.30 <sup>a</sup>	14.8%	2.272 <sup>b</sup>	3.8%	2.647 <sup>b</sup>			4.2%
			2.272 <sup>c</sup>	3.8%	2.620 <sup>c</sup>			5.3%
4	1395.55		2.340		2.792	13.605	8.554	
	1627.35 <sup>a</sup>	14.2%	2.253 <sup>b</sup>	3.8%	2.680 <sup>b</sup>			4.1%
			2.256 <sup>c</sup>	3.7%	2.647 <sup>c</sup>			5.4%
5	1712.20		2.322		2.823	13.555	10.786	
	1981.78 <sup>a</sup>	13.5%	2.236 <sup>b</sup>	3.8%	2.709 <sup>b</sup>			4.2%
			2.243 <sup>c</sup>	3.5%	2.672 <sup>c</sup>			5.6%

<sup>a</sup>Rao, T.V.R. (1983), <sup>b</sup>Rao, T.V.R. (1983), <sup>b</sup>Lakshman and Rao's method. <sup>c</sup>Rao, T.V.R. (1983), Morse method.

Table 4. Values of the eigenvalue  $E_v$ , the rotational constant  $B_v$ , the centrifugal distortion constants  $D_v$  (in  $\text{cm}^{-1}$ ) and the abscissas of the turning points (in  $\text{\AA}$ ) of the  $(2)^2\Pi$  state of CaCl molecule up to  $v=10$

v	$E_v(\text{cm}^{-1})$		$R_{\min}(\text{\AA})$		$R_{\max}(\text{\AA})$		$B_v \times 10^2 (\text{cm}^{-1})$	$D_v \times 10^8 (\text{cm}^{-1})$
		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$		$\left[\frac{\Delta X}{X}\right]$		
0	141.78		2.498		2.762		12.989	15.916
	167.65 <sup>a</sup>	15.4%	2.449 <sup>b</sup>	2.0%	2.589 <sup>b</sup>	6.6%		
			2.445 <sup>c</sup>	2.1%	2.592 <sup>c</sup>	6.5%		
1	405.64		2.479		2.822		12.578	7.534
	500.85 <sup>a</sup>	17.0%	2.395 <sup>b</sup>	3.5%	2.650 <sup>b</sup>	6.4%		
			2.398 <sup>c</sup>	3.3%	2.653 <sup>c</sup>	6.3%		
2	695.61		2.447		2.871		12.657	15.707
	831.25 <sup>a</sup>	16.3%	2.364 <sup>b</sup>	3.5%	2.695 <sup>b</sup>	6.5%		
			2.367 <sup>c</sup>	3.3%	2.698 <sup>c</sup>	6.4%		
3	987.92		2.428		2.910		12.463	5.0478
	1158.85 <sup>a</sup>	14.7%	2.339 <sup>b</sup>	3.8%	2.732 <sup>b</sup>	6.5%		
			2.343 <sup>c</sup>	3.6%	2.736 <sup>c</sup>	6.3%		
4	1277.18		2.410		2.948		12.407	16.609
	1483.65 <sup>a</sup>	13.8%	2.319 <sup>b</sup>	3.9%	2.766 <sup>b</sup>	6.5%		
			2.323 <sup>c</sup>	3.7%	2.770 <sup>c</sup>	6.4%		
5	1569.69		2.395		2.982		12.36	6.3125
	1805.65 <sup>a</sup>	13.0%	2.301 <sup>b</sup>	4.0%	2.797 <sup>b</sup>	6.6%		
			2.305 <sup>c</sup>	3.9%	2.801 <sup>c</sup>	6.4%		
6	1895.10		2.380		3.014		12.203	12.43
	2124.85 <sup>a</sup>	11.2%	2.285 <sup>b</sup>	4.1%	2.827 <sup>b</sup>	6.6%		
			2.290 <sup>c</sup>	3.9%	2.831 <sup>c</sup>	6.4%		
7	2189.862		2.367		3.045		12.198	13.208
8	2445.9		2.355		3.076		12.045	8.8098
9	2800.543		2.344		3.113		11.926	16.932
10	3145.834		2.334		3.138		11.87	8.7785

<sup>a</sup>Rao (1983), <sup>b</sup>Rao (1983), Lakshman & Rao's method, <sup>c</sup>Rao (1983), Morse method.

The dipole moment is a fundamental electrostatic property for the description of numerous physical phenomena. Our calculated values of the static dipole moments for the considered lowest-lying electronic as a function of the internuclear distance are given in Figures 4-6. By comparing the positions of points of interaction of these curves with those of the potential energy curves (Figures 1-3) one can notice the agreement between the 3 positions of the avoided crossing of the PECs and the crossings of dipole moment curves (Table 1). This agreement may confirm the validity and the accuracy of the calculation of the studied electronic states.

#### 4. Conclusions

In summary, the potential energy curves for the ground and 14 low-lying excited electronic states of CaCl molecule have been reported at the MRCI level. The present results show that the PECs of excited states intercross one another in several places, which make the shapes of some PECs changed. Our calculated spectroscopic parameters and vibrational levels are in good agreement with the experimental data available in literature. The comparison of these data with the theoretical results in the literature shows a very good agreement using some techniques of calculation while the agreement deteriorates for other techniques even for the same electronic state. However, there is no comparison for some molecular properties predicted for the investigated electronic states by the present work since they are calculated here for the first time. So, we believe that the present results for both the ground state and low-lying excited electronic states based, on *ab initio* calculations, can encourage more investigations for the molecule CaCl.

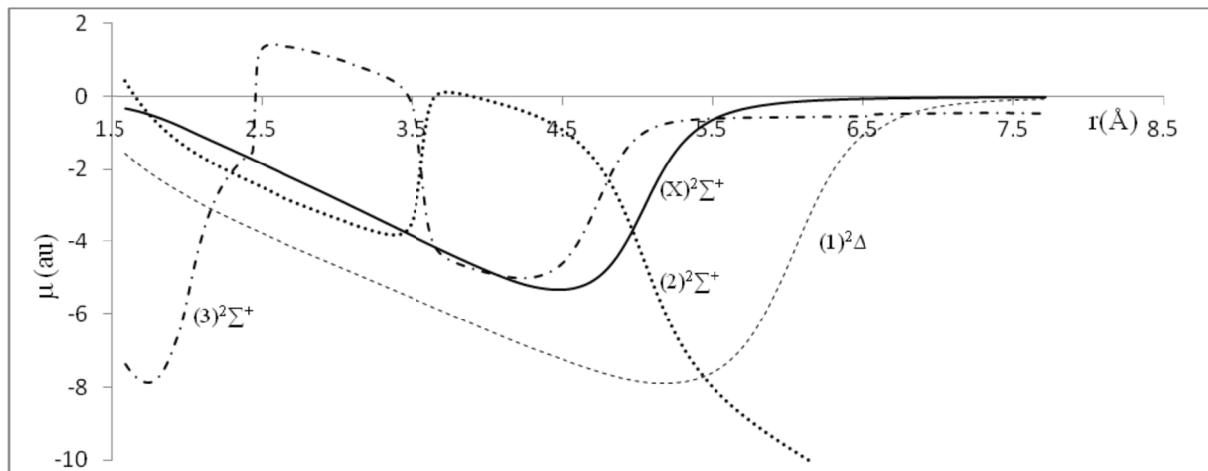


Figure 4. Permanent dipole moment, calculated by MRCI method, for the  $^2\Sigma^\pm$  and  $^2\Delta$  states of the molecule CaCl

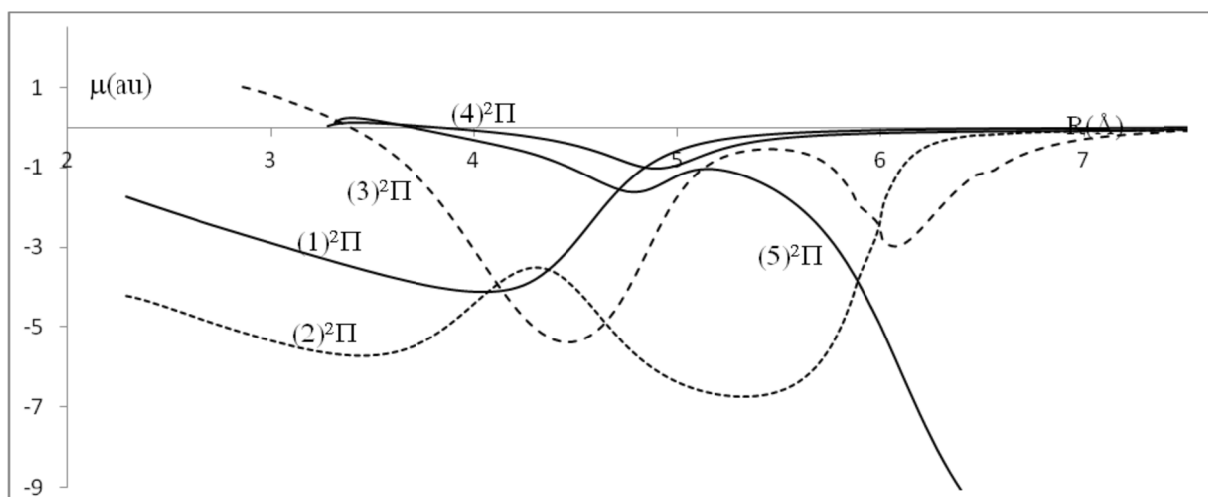


Figure 5. Permanent dipole moment, calculated by MRCI method, for the  $^2\Pi$  states of the molecule CaCl

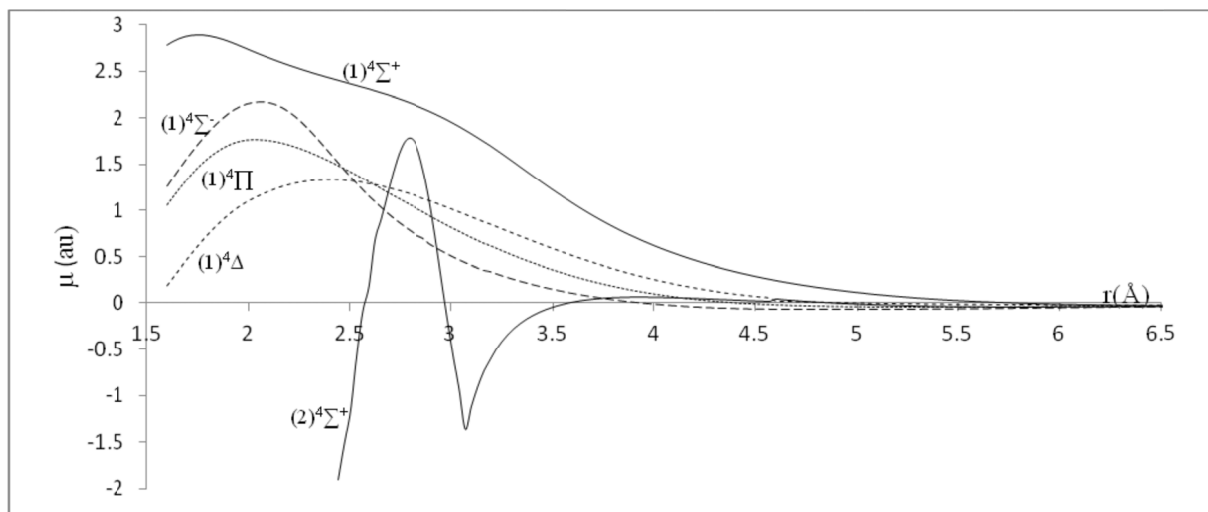


Figure 6. Permanent dipole moment, calculated by MRCI method, for the  $^4\Sigma^\pm$ ,  $^4\Delta$ , and  $^4\Pi$  states of the molecule CaCl

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