

Electronic Structure and Dipole Moment Calculations of the Electronic States of the Molecule BeCl

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Received: January 27, 2017

Accepted: February 16, 2017

Online Published: May 14, 2017

doi:10.5539/mas.v11n6p90

URL: <https://doi.org/10.5539/mas.v11n6p90>

Abstract

The electronic structure of the molecule BeCl have been investigated by using the Complete Active Space Self Consistent Field (CASSCF) with Multireference Configuration Interaction MRCI+Q (singly and doubly excitation with Davidson corrections). The potential energy curves, in terms of the internuclear distance R , have been calculated for 13 doublet and 14 quartet electronic states in the representation $^{2s+1}\Lambda^{(+/-)}$ of the molecule BeCl. The internuclear distance at equilibrium R_e , the electronic energy with respect to the ground state T_e , the harmonic frequency ω_e , the rotational constants B_e and the permanent dipole moment have been calculated for the bound electronic states. The Franck-Condon factor is calculated for the electronic transition between the two electronic states $X^2\Sigma^+-(1)^2\Pi$. Since there is limited data are published in literature, twenty-two new electronic states have been investigated here for the first time for the molecule BeCl. The comparison between our calculated values and those available in the literature shows a very good good agreement.

Keywords: *ab initio* calculation, permanent dipole moments, electronic structure, spectroscopic constants, potential energy curves. Franck-Condon factor

1. Introduction

The alkaline-earth monohalide received a considerable attention from experimentalists since the early thirties (Fredrickson and Hogan Jr 1934). A reinvestigation, and further refinement, of the spectroscopic data of the molecule BeCl have been provided by (Novikov and Tunitskii 1960), (Hildenbrand 1969) and (Colin, Carleer, & Prevot 1972). Recently more experimental data on this molecule has been provided by (Farber & Srivastava 1974), (Carleer, Burtin, & Colin 1977), (Subbaram, Vasudeo, & Jones 1975), (Varma & Jha 1979), and (Knight Jr., Wise, Childers, Daasch, & Davidson, 1981). In an Early attempts, a limited number of low-lying electronic states of the molecule BeCl has been calculated along with the radiative lifetimes and the Franck-Condon factors (Singh & Prabhuram 1975), (Varma & Jha 1981), (Montagnani, Riani, & Salvetti 1983), (Langhoff, Bauschlicher Jr., & Partridge 1986), (Langhoff, Bauschlicher Jr., Partridge, & Ahlrichs 1986), (Bruna & Grein 2001), (Behere, Saksena, Deo, & Jadhav 2006), (Vasiliu, Feller, Gole, & Dixon 2010).

Shuman et al. (Shuman, Barry, & DeMille 2010) introduce the first direct cooling of a polar molecule (SrF) by using an optical cycling scheme with Doppler and Sisyphus cooling forces. This significant innovation needs a deep knowledge of the electronic structure and its ro-vibrational energy levels of the ultracold candidate molecule. Moreover, highly diagonally distributed Franck-Condon factors (FCFs) and the short radiative lifetimes (between 10^{-6} and 10^{-9} s) are needed for these ultracold molecules. While the FCF calculation is based on the accurate potential energy curve of two electronic states, the radiative lifetimes needs the calculation of the dipole moment.

DeMille (DeMille2002) has detailed a prototype design for quantum computation using ultracold polar molecules, trapped in a one-dimensional optical lattice, partially oriented in an external electric field, and coupled by the dipole-dipole interaction. This offers a promising platform for quantum computing because scale-up appears feasible to obtain large networks of coupled qubits.

In order to provide an accurate global picture of a manifold of electronic states of BeCl molecule and quantitatively account of the observed spectra we present in this work, the theoretical electronic structure of BeCl molecule. By using *ab-initio* method 13 doublet and 14 quartet electronic states have been investigated. The Potential energy curves (PECs) have been plotted, the spectroscopic constants T_e , ω_e , $\omega_e x_e$, B_e , the

internuclear distances R_e and the electronic static dipole moments have been calculated. The Franck-Condon factors have been calculated for electronic transitions with the discussion on the feasibility of laser cooling of the BeCl molecule

2. Method

By using Complete Active Space Self Consistent Field (CASSCF) procedure followed by a multireference configuration interaction (MRCI+Q with Davidson correction), we investigated the low-lying double and quartet electronic states of the molecule BeCl. These calculations have been performed by the computational chemistry program MOLPRO (Molpro) using the graphical user interface GABEDIT (Allouche 2011). The beryllium and the chlorine atoms are treated in all electrons schemes by using the basis sets cc-pVTZ;c and aug-cc-pVQZ;c for Be and Cl atoms respectively with the s , p , d orbitals for the 2 atoms. The active space has been identified in the C_{2v} symmetry: 10σ (Be: $1s$, $2s$, $2p_0$, $3s$; Cl: $1s$, $2s$, $2p_0$, $3s$, $3p_0$, $4s$), 3π (Be: $2p_{\pm 1}$; Na: $2p_{\pm 1}$, $3p_{\pm 1}$) distributed into irreducible representation of the C_{2v} group: noted by [10,3,3,0]. Being an heteronuclear diatomic molecule, BeCl is of $C_{\infty v}$ point group symmetry; however, MOLPRO software can only make use of Abelian point groups which means that $C_{\infty v}$ will be treated using the C_{2v} point group placing the molecule along the $+z$ -axis and keeping Be at the origin.

3. Results

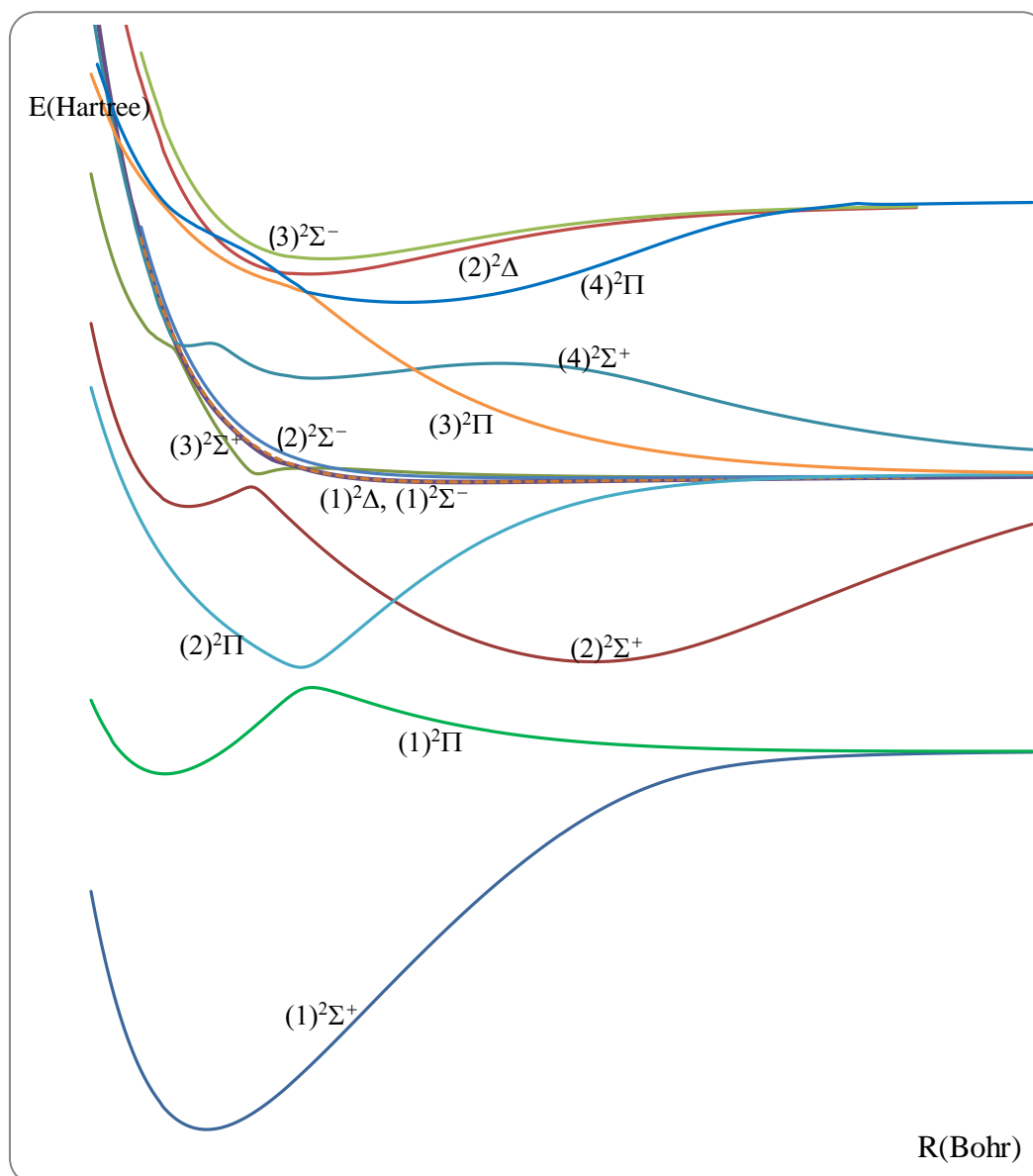


Figure 1. Potential energy curves of the ${}^2\Sigma^{\pm}$, ${}^2\Pi$ and ${}^2\Delta$ states of the molecule BeCl

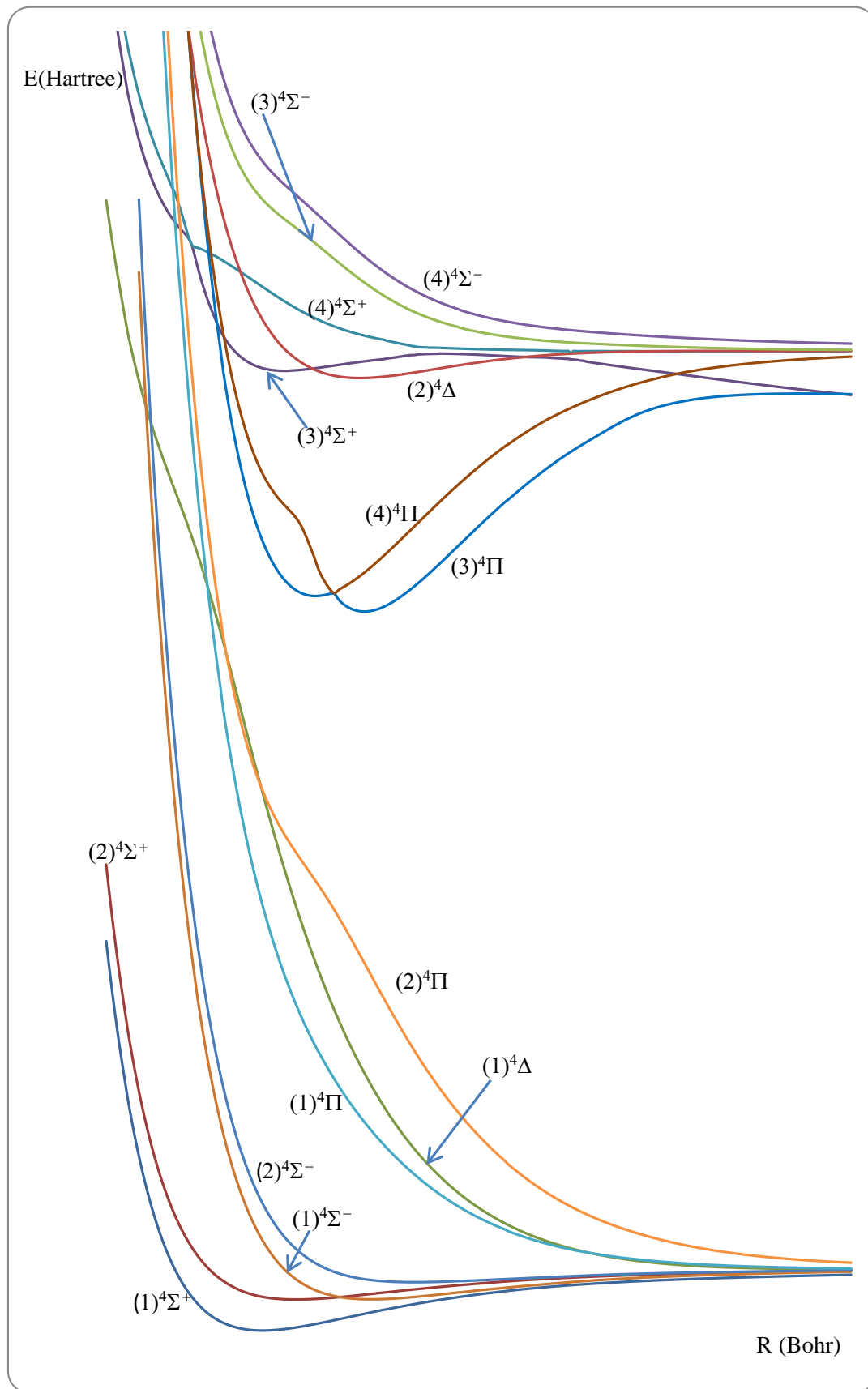


Figure 2. Potential energy curves of the $4\Sigma^\pm$, 4Π , and 4Δ states of the molecule BeCl

3.1 Potential Energy Curves and Spectroscopic Constants

The potential energy curves (PECs) for the 27 doublet and quartet electronic states, in the representation $^{2s+1}\Lambda^{(\pm)}$, of the molecule BeCl were generated using the MRCI+Q for 303 internuclear distances calculations in the range $1.442\text{\AA} \leq R_e \leq 4.452\text{\AA}$ (Figs. (1-2)). The spectroscopic constants ω_e , T_e , and B_e have been obtained by fitting the calculated points around the internuclear distance at equilibrium R_e of the investigated electronic states into a polynomial in R . The comparison of these values with those available in literature (Barreto de Lima & Ornellas 2013), (Vasiliu, Feller, Gole, & Dixon 2010), (Colin, Carleer, & Prevot 1972), and (Carleer, Burtin, & Colin 1977) are given in Table 1.

Table 1. Spectroscopic constants of the molecule BeCl

State	T_e cm ⁻¹	$\Delta T_e/T_e$ %	R_e Bohr	$\Delta R_e/R_e$ %	B_e cm ⁻¹	$\Delta B_e/B_e$ %	ω_e cm ⁻¹	$\Delta\omega_e/\omega_e$ %
$X^2\Sigma^+$	0.0 ^a		1.802		0.7140		838.6	
Ref. ^{theo} [22]	0.0 ^b		1.781	1.16	0.7322	2.55	849.2	1.26
Ref. ^{theo} [23]	0.0 ^c		1.798	2.22			845.5	0.82
Ref. ^{exp} [24]	0.0 ^d		1.797	0.28	0.7285	2.03	847.19	1.02
(1) ² Π	28483 ^a		1.839		0.6935		813.4	
Ref. ^{theo} [22]	28464 ^b	0.07	1.814	1.36	0.7136	2.90	828.7	1.88
Ref. ^{exp} [24]	27992.9 ^c	1.72	1.815	1.30	0.7094	2.29	822.1	1.07
(2) ² Π	37051 ^a		2.271		0.4548		939.6	
Ref. ^{theo} [22]	38801 ^b	4.72	2.303	1.41	0.4435	2.48	834.87	11.2
(1) ⁴ Σ ⁺	49884.4 ^a		2.272		0.4539		275.9	
(2) ² Σ ⁺ (ext.)	37458 ^a		3.047		0.2527		344.1	
Ref. ^{exp} [24]	39438 ^b	5.02	3.073	0.85	0.2490	1.46	331.3	3.72
(2) ² Σ ⁺ (int.)	49894 ^a		1.754		0.7623		847.2	
Ref. ^{theo} [22]	47818 ^d	4.16	1.722	1.82	0.7948	4.26	974.4	15.01
Ref. ^{exp} [25]	48773 ^e	2.25	1.742	0.68	0.7751	1.68	952.5	12.42
(1) ⁴ Σ ⁺	51169.7 ^a		2.414		0.4022		190.7	
(2) ⁴ Σ ⁺	51178.0 ^a		2.415		0.4017		191.6	
(4) ² Σ ⁺	51851.5 ^a		2.635		0.3358		104.5	
(1) ² Δ	51855.1 ^a		2.641		0.3355		104.4	
(2) ⁴ Σ ⁻	51887.0 ^a		2.603		0.3460		127.1	
(1) ² Σ ⁻	52192.6 ^a		3.004		0.2958		91.0	
(4) ² Π	66242.3 ^a		2.607		0.3453		275.5	
(2) ² Δ	68510.1 ^a		2.141		0.5119		358.0	
(3) ² Σ ⁻	69725.7 ^a		2.190		0.4891		365.6	

^aPresent work, ^b(Barreto de Lima & Ornellas 2013), ^c(Vasiliu, Feller, Gole, & Dixon 2010), ^d(Colin, Carleer, & Prevot 1972), and ^e(Carleer, Burtin, & Colin 1977).

The comparison of our calculated values of the constants T_e , R_e , B_e , and ω_e , with the experimental data given in literature (Colin, Carleer, & Prevot 1972), and (Carleer, Burtin, & Colin 1977) for the three electronic states $X^2\Sigma^+$, (1)²Π, and (2)²Σ⁺ shows a very good agreement. The relative differences are 1.72%(Colin, Carleer, &

Prevot)(1)²Π)≤ΔT_e/T_e≤5.02% (Colin, Carleer, & Prevot), (2)²Σ⁺)0.28% (Colin, Carleer, & Prevot) X²Σ⁺≤ΔR_e/R_e≤1.30% (Colin, Carleer, & Prevot)(1)²Π), 1.68% (Carleer, Burtin, & Colin 1977) (2)²Σ⁺)≤ΔB_e/B_e≤2.29 (Colin, Carleer, & Prevot) (1)²Π), 1.02% (Colin, Carleer, & Prevot) X²Σ⁺)≤Δω_e/ω_e≤3.72 (Colin, Carleer, & Prevot) (2)²Σ⁺), except value of ω_e given by (Carleer, Burtin, & Colin 1977) for the electronic state (2)²Σ⁺ where the relative difference is 12.42%. While the comparison with the theoretical values in literature (Barreto de Lima & Ornellas 2013), (Vasiliu, Feller, Gole, & Dixon), shows 0.07%(Barreto de Lima & Ornellas)(1)²Π)≤ΔT_e/T_e≤4.72%(Barreto de Lima & Ornellas)(2)²Π), 1.16%(Barreto de Lima & Ornellas)X²Σ⁺≤ΔR_e/R_e≤2.22%(Vasiliu, Feller, Gole, & DixonX²Σ⁺), 2.48%(Barreto de Lima & Ornellas)(2)²Π)≤ΔB_e/B_e≤4.26(Barreto de Lima & Ornellas)(1)²Σ⁺), 0.82%([23] X²Σ⁺)≤Δω_e/ω_e≤11.2(Barreto de Lima & Ornellas)(2)²Π). One can notice that our calculated vlues of the spectroscopic constants are in better agreement with experimental data then the theoretical values givnen in literature for these constants. With this agreement with literature values, we can predict the accuracy of the spectroscopic constants of the new electronic states investigated for the first time in the present work.

3.2 Permanent Dipole Moment

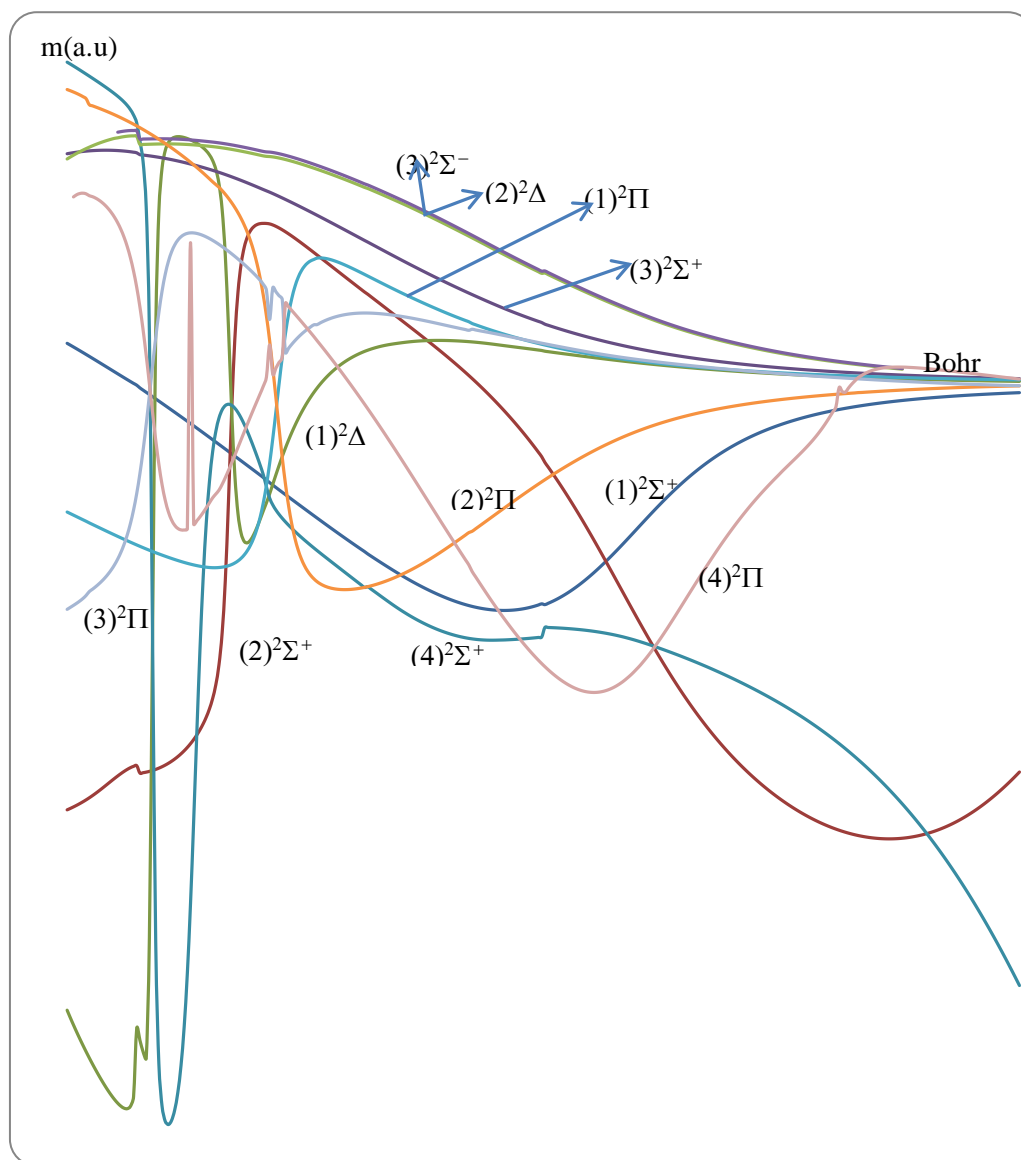


Figure 3. Permanent dipole cuves of the electronic states ²Σ[±], ²Δ and ²Π of the molecule BeCl

The permanent dipole moment (PMD) is a fundamental electrostatic property of a neutral molecule. Its importance is lying in the accurate predictions of transition dipoles and the description of numerous physical phenomena. By taking the Be atom at the origin and chlorine atom along the internuclear Z-axis, we present in Figs (1-2) the calculated values of the permanent dipole moment in term of the internuclear distance R.

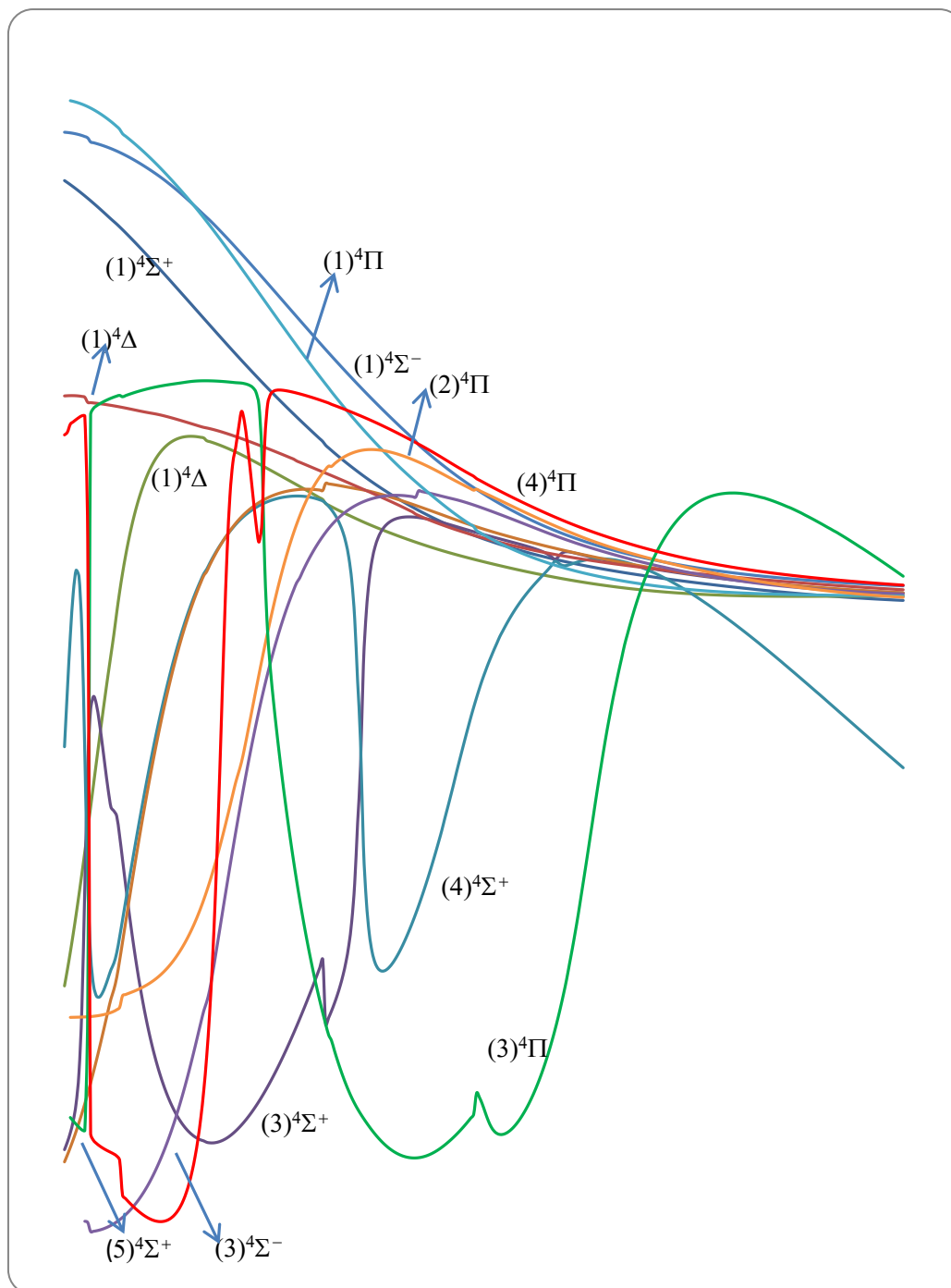


Figure 4. Permanent dipole cuves of the electronic states ${}^4\Sigma^\pm$, ${}^4\Delta$, ${}^4\Pi$ and of the molecule BeCl

The polarity of the states with their interactions and the bond nature are discussed by the investigation of these PDM curves. One can notice that, as the internuclear distance increases there are two types of curves: *i*) dipole moment curves in the positive region which are corresponding to an ionic structure of $\text{Be}^{\delta-}\text{Cl}^{\delta+}$ type, *ii*) curves passing from one region to another by changing the ionic structure. At large internuclear distance R there are also two types of curves: *i*) dipole moment curves tend smoothly to zero where the molecule is dissociating into

natural fragments, *ii*) dipole moment curves, for the other electronic states, increase in the negative region which point out polarized states that dissociate into ionic fragments. The sharp change in the directions of the PDM curves indicates a reverse in the polarity of the atoms where we can find an avoided crossing of the potential energy curves at the same position of the internuclear distance. From this agreement, we can confirm the validity and the accuracy of the calculation of the studied excited electronic states.

3.3 Franck-Condon Factor

The overlap of the vibrational wave functions is described by the calculation of the Franck-Condon Factor (FCF). For a spontaneous radiative transition, the calculation of this factor is essential to identify the optimal electronic transition for laser cooling. The calculated values of the FCF for the electronic transition $X^2\Sigma^+-(1)^2\Pi$ have been done by using the LEVEL8.2 program (A computer program). These values are given in Table 2 and represented in Fig.5

Table 2. Values of the Franck-Condon Factor for the electronic transition $X^2\Sigma^+-(1)^2\Pi$

$(1)^2\Pi (v') \leftrightarrow X^2\Sigma^+ (v) ([-n]=10^n)$											
v'/v	0	1	2	3	4	5	6	7	8	9	10
0	9.39[-1]	6.04[-2]	7.38[-4]	2.08[-6]	1.70[-8]	4.76[-9]	1.28[-8]	1.04[-9]	4.92[-10]	6.63[-10]	1.52[-10]
1	5.75[-2]	8.23[-1]	1.17[-1]	2.26[-3]	1.13[-5]	2.05[-10]	6.72[-9]	2.48[-8]	2.44[-9]	2.62[-9]	6.37[-9]
2	3.39[-3]	1.06[-1]	7.16[-1]	1.70[-1]	4.48[-3]	3.01[-5]	7.33[-8]	2.66[-9]	1.50[-8]	3.23[-10]	3.00[-8]
3	2.29[-4]	9.42[-3]	1.46[-1]	6.19[-1]	2.18[-1]	7.42[-3]	5.88[-5]	2.70[-7]	2.66[-8]	2.44[-8]	5.15[-9]
4	1.81[-5]	8.65[-4]	1.75[-2]	1.77[-1]	5.30[-1]	2.64[-1]	1.14[-2]	9.10[-5]	1.60[-7]	4.84[-8]	6.29[-7]
5	1.83[-6]	9.30[-5]	2.03[-3]	2.72[-2]	2.02[-1]	4.44[-1]	3.09[-1]	1.69[-2]	1.48[-4]	9.60[-7]	3.78[-7]
6	3.32[-7]	1.24[-5]	2.73[-4]	3.87[-3]	3.87[-2]	2.21[-1]	3.60[-1]	3.51[-1]	2.47[-2]	3.48[-4]	2.80[-5]
7	1.04[-7]	2.28[-6]	4.38[-5]	6.12[-4]	6.53[-3]	5.19[-2]	2.34[-1]	2.79[-1]	3.88[-1]	3.73[-2]	1.28[-3]
8	3.32[-8]	5.85[-7]	8.19[-6]	1.07[-4]	1.14[-3]	1.02[-2]	6.48[-2]	2.39[-1]	1.90[-1]	4.18[-1]	6.53[-2]
9	6.93[-9]	1.55[-7]	1.68[-6]	1.92[-5]	2.13[-4]	1.87[-3]	1.44[-2]	7.17[-2]	2.19[-1]	5.97[-2]	3.79[-1]
10	7.97[-10]	2.53[-8]	2.59[-7]	2.78[-6]	3.10[-5]	2.85[-4]	2.21[-3]	1.32[-2]	4.77[-2]	7.68[-2]	2.80[-2]

The large diagonal values of the Franck-Condon factor for the transition $X^2\Sigma^+ (v'=0) \leftrightarrow (1)^2\Pi (v=0)$ show that the molecule BeCl can be considered as a good candidate for laser cooling through $X^2\Sigma^+ - (1)^2\Pi$ electronic transition.

4. Conclusion

From an initio calculation the potential energy curves of 27 electronic states have investigated by using the complete active space self-consistent field (CASSCF) with multireference configuration interaction MRCI+Q (singly and doubly excitation with Davidson corrections). The spectroscopic constants R_e , ω_e , T_e , and B_e are determined for the investigated bound electronic states. The permanent dipole moment have been calculated for the investigated electronic states and plotted in terms of the internuclear distance R . The calculated values of the FCF for the transition $X^2\Sigma^+-(1)^2\Pi$ shows that the molecule BeCl is a good candidate for a laser cooling for this transition. Twenty-three new electronic states have been investigated in the present work for the first time. The confirmation of these theoretical investigated data can be done by a future experiment for these electronic states of the molecule BeCl.

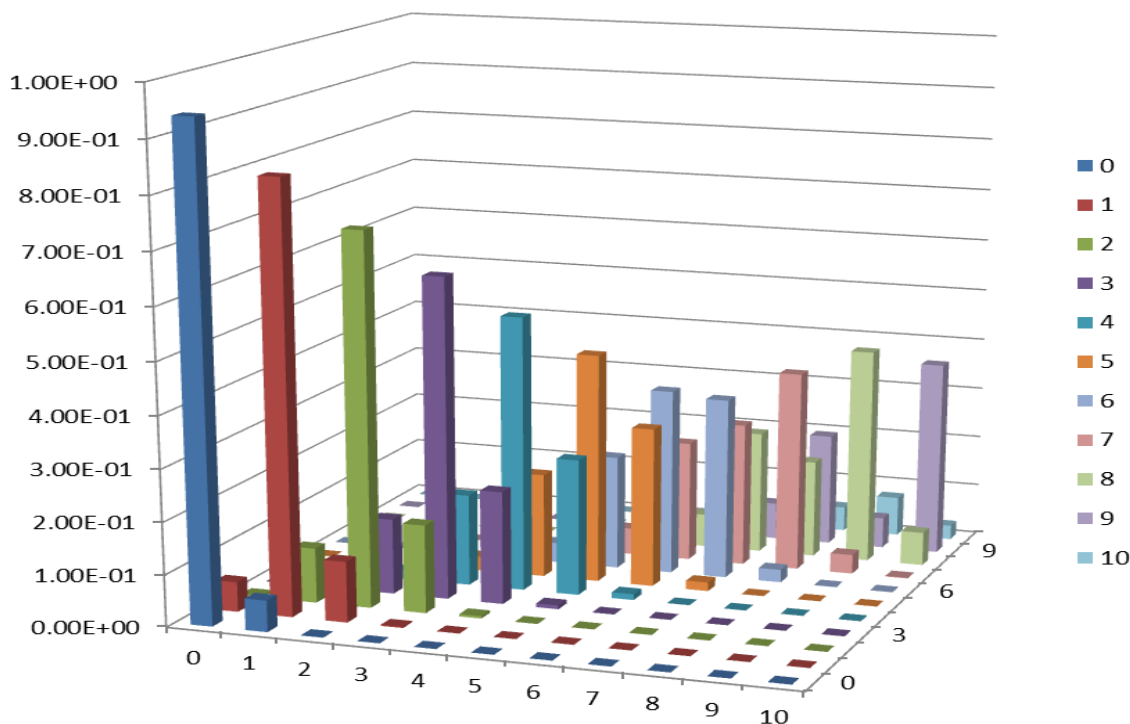


Figure 5. Franck-Condon Factor for the electronic transition $X^2\Sigma^+-(1)^2\Pi$ in terms of the vibrational levels v and v'

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