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Theoretical Study of the LiCs Molecule: Adiabatic and Diabatic Potential Energy and Dipole Moment

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For nearly all the states dissociating into Cs (6s, 6p, 5d, 7s, 7p, 6d, 8s) and Li (2s, 2p, 3s), we present an extensive adiabatic study for $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ symmetries of the LiCs molecule. We have used an ab initio approach based on nonempirical pseudopotentials, parametrized l -dependent polarization potentials, and full configuration interaction calculations. A diabatisation procedure based on the effective Hamiltonian theory and an effective metric is used to produce the quasi-diabatic potential energy for all studied states. The spectroscopic constants (R_e , D_e , T_e , ω_e , $\omega_e x_e$, and B_e) of these states are derived and compared with the available theoretical and experimental works. In addition to the potential energies, accurate permanent and transition dipole moment have been determined for a wide range of internuclear distances. The adiabatic permanent dipole moment for the first 10 $^1\Sigma^+$ electronic states has revealed ionic characters relating to electron transfer and yielding both Li^-Cs^+ and Li^+Cs^- arrangements. The quasi-diabatic permanent moments show linear behaviors, especially at intermediate and large distance. The transition dipole moment between neighbor states has revealed many peaks located around the avoided crossing positions.

I. Introduction

During the past decade, an important effort has been devoted in the development of ultrashort and intense laser pulses, opening a new research domain in molecular dynamics and molecular spectroscopy. Such important theoretical and experimental efforts are motivated by the possible applications such as manipulation and controlling of ultracold chemical reactions,^{1–3} ultracold molecular collision dynamics,^{4–7} quantum computing,^{8,9} and experimental preparation of few-body quantum effects¹⁰ (such as Efimov states), where the aim is to prepare molecules in definite quantum states with respect to the center of mass, electronic, rotational, and vibrational motions.¹¹ Furthermore, it is expected that the long-range interaction will introduce new important physical phenomena. At the heart of such research has been the study of the effects of strong electric fields on the vibrational dynamics¹² of alkali dimers.

Several theoretical studies of the electronic structure of these systems have been performed in our group for LiCs,¹³ LiNa,^{14,15} and NaCs.¹⁶ Other authors were interested in studying the heteronuclear alkali dimers using various quantum chemistry methods to determine the potential energy curves of the ground and excited states of RbCs,^{17–19} NaRb and LiRb,²⁰ NaCs, LiCs and CsK,²¹ KRb,²² LiK,²³ NaK,^{24,25} and LiNa.^{26,27}

Several theoretical^{12,21,28–32} and experimental^{7,11,33–37} studies have been performed for the LiCs molecule. The first theoretical study of the LiCs molecule was made by Igel-Mann et al.²⁹ based on pseudopotential and CI calculations. They have determined the spectroscopic constants for the ground state. Korek et al.²¹ have made an ab initio calculation for the LiCs

molecule, where they determined the potential energy curves for 7, 5, and 2 states of, respectively, $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ symmetries. Recently, the lowest 55 states of the Ω -representation (including the spin–orbit effect) of the LiCs molecule have been investigated by Elkork et al.³⁸ The LiCs molecule was also treated by many authors such as Gonzalez-Ferez et al.,³⁰ who investigated the effect of strong electric fields on the rovibrational dynamics of LiCs in its $^1\Sigma^+$ electronic ground state. Aymar and Dulieu²⁸ performed an extensive ab initio study on mixed alkali pairs in order to determine accurate potential energy and permanent dipole moments of the lowest $^1\Sigma^+$ states using extended basis sets. Recently, theoretical coupled cluster (CC) calculations have been performed by Fleig and Sørensen.³¹ The aim of their work was to test and apply a relativistic four-component multireference CC method³¹ on the ground state of LiCs. It represents a general-order multireference CC approach in the four-component relativistic framework using different relativistic Hamiltonians and varying levels of electron correlation, where 0, 10, and 22 electrons were treated in the CI calculations. Recently Smirnov¹² has calculated vibrational, rotational, and centrifugal spectroscopic constants for the ground state by introducing an analytical form for the potential energy of Korek et al.²¹ A recent theoretical study of the LiCs molecule was made by Krems,⁷ who demonstrated that elastic collisions of ultracold atoms in a heteronuclear collision can be manipulated by laboratory dc fields. More recently, Sørensen et al.³² have investigated the ground state of the LiCs molecule using a new general-order CC method applied in the framework of the spin-free Dirac formalism. The authors presented a systematic study of electron correlation and relativistic effects on the spectroscopic and electric properties of the LiCs molecule in its electronic ground state.

The first observation of ultracold LiCs molecules was reported by Wang and Stwalley³⁵ and Kraft et al.¹¹ in 2006; and Staunum

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et al.³³ in 2007 presented the first high-resolution spectroscopic study for the LiCs molecule. Stein et al.³⁶ investigated the $1^1\Pi$ (B) and $2^1\Pi$ (D) excited states using the same technique in their previous paper.³³

The present work completes our study on the LiCs alkali molecule beyond the Born–Oppenheimer approximation published in the AIP Conference Proceeding¹³ as an extended abstract and where only the spectroscopic data of the first $10^1\Sigma^+$ states were reported. The used methods and a generalization to the remaining symmetries are presented in this article in further details. In this context, we have calculated the adiabatic and quasi-adiabatic potential energy curves of $1-10^1\Sigma^+$, $1-6^1\Pi$, and $1-3^1\Delta$ states dissociating into Cs(6s, 6p, 5d, 7s, 7p, 6d, 8s) and Li (2s, 2p, 3s), and derived their spectroscopic constants. A similar study on this system was achieved previously by Korek et al.,²¹ although it was focused on the adiabatic states and presented the potential energy curves and the spectroscopic constants of $1-7^1\Sigma^+$, $1-5^1\Pi$, and $1-2^1\Delta$ states were presented. Our study is generalized for some higher excited states, but also for larger and denser internuclear distance grid. Furthermore, we have determined the adiabatic and quasi-adiabatic permanent dipole moment for all studied states and the transition dipoles between neighbor states for each symmetry.

This paper is organized as follows. In Section 2, we present the computational method and give numerical details. In Section 3, which is divided into three parts, we present the adiabatic potential energy curves and their spectroscopic constants for the ground and numerous excited states of $1^1\Sigma^+$, $1^1\Pi$, and $1^1\Delta$ symmetries; the quasi-adiabatic potential energy curves; and finally calculations of the permanent and transition dipole moments (the latter between neighboring states). In Section 4, we summarize our conclusion.

II. Methods

II.1. Computational Details. The Cs and Li atoms are treated through one-electron pseudopotentials proposed by Durand and Barthelat³⁹ and are used in many previous works.^{40–46} For the interaction between the polarizable Li^+ and Cs^+ cores with the valence electrons, a core polarization potential V_{CPP} is used according to the operatorial formulation of Müller et al.⁴⁷

$$V_{\text{CPP}} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} \vec{f}_{\lambda} \cdot \vec{f}_{\lambda}$$

where α_{λ} is the dipole polarizability of the core λ , and \vec{f}_{λ} is the electric field produced by valence electrons and all other cores on the core λ .

$$\vec{f}_{\lambda} = \sum_i \frac{\vec{r}_{i\lambda}}{r_{i\lambda}^3} F(r_{i\lambda}, \rho_{\lambda}) - \sum_{\lambda' \neq \lambda} \frac{\vec{R}_{\lambda'\lambda}}{R_{\lambda'\lambda}^3} Z_{\lambda'}$$

where $r_{i\lambda}$ is a core–electron vector and $R_{\lambda'\lambda}$ is a core–core vector.

According to the formulation of Foucault et al.,⁴⁸ the cutoff function $F(r_{i\lambda}, \rho_{\lambda})$ is taken to be a function of l in order to treat separately the interaction of valence electrons of different spatial symmetry and the core electrons. It has a physical meaning of excluding the valence electrons from the core region for calculating the electric field. In the formalism of Müller et al.,⁴⁷ the cutoff function is unique for a given atom and is generally adjusted to reproduce the atomic energy levels for the lowest states of each symmetry.

TABLE 1: l-Dependent Cutoff Radii (in Bohr) for Cs and Li Atoms

	Li	Cs
s	1.434	2.7923
p	0.979	2.667
d	0.600	2.89575
f	0.400	2.81

TABLE 2: Asymptotic Energy of LiCs Electronic States (au)

asymptotic molecular states	expt. ⁴⁹	This work ΔE (cm ^{−1})
Li(2s) + Cs(6s) ($1^1\Sigma^+$)	−0.341 242	−0.341 241 0.219
Li(2s) + Cs(6p) ($2^1\Sigma^+$, $1^1\Pi$)	−0.288 6255	−0.288 626 0.110
Li(2s) + Cs(5d) ($3^1\Sigma^+$, $2^1\Pi$, $1^1\Delta$)	−0.274 9109	−0.274 91 0.198
Li(2p) + Cs(6s) ($4^1\Sigma^+$, $3^1\Pi$)	−0.273 335	−0.273 334 0.219
Li(2s) + Cs(7s) ($5^1\Sigma^+$)	−0.256 7859	−0.256 774 2.414
Li(2s) + Cs(7p) ($6^1\Sigma^+$, $4^1\Pi$)	−0.241 5222	−0.241 548 5.487
Li(2s) + Cs(6d) ($7^1\Sigma^+$, $5^1\Pi$, $2^1\Delta$)	−0.238 20065	−0.237 88 70.232
Li(2s) + Cs(8s) ($8^1\Sigma^+$)	−0.230 4457	−0.230 421 5.267
Li(2p) + Cs(6p) ($9^1\Sigma^+$, $6^1\Pi$, $3^1\Delta$)	−0.220 7185	−0.220 719 0.110
Li(3s) + Cs(6s) ($10^1\Sigma^+$)	−0.217 282	−0.217 201 17.777

Furthermore, the self-consistent field calculation (SCF) is followed by a full valence configuration interaction (CI) calculation using the CIPCI algorithm of the Laboratoire de Chimie et Physique Quantique de Toulouse.

For Cs, we have used a 8s/5p/5d/2f Gaussian basis set taken from ref 17, and for the Li we have used the same basis set of Gaussian-type orbital (GTOs) as in our previous works.^{40–46} The core dipole polarizability of Cs and Li are, respectively, 15.81 and 0.1915 a₀³. The cutoff radii (ρ) for the lowest s, p, d, and f one-electron valence orbitals are reported in Table 1. Table 2 presents a comparison between our calculation and the experimental⁴⁹ values of ionization potential (IP) and atomic energy levels. The difference does not exceed 70.3 cm^{−1}, which is found for the Cs(6d) atomic limit. It is important to note that the ground state atomic energy (for Li or Cs) is taken as the negative value of the experimental ionization energy. Therefore, the difference energy between the atomic levels and the ground state is added to the latter value in order to find the atomic energy for the excited states. The basis sets for Cs and Li were optimized previously^{17,40–46} in order to get the best agreement with the experiment.

II.2. Diabatisation Method. The diabatisation method has been presented in details previously^{50–53} and these applications have shown its efficiency. It was tested, first, for the CsH molecule⁵³ and used later for LiH,^{51,54–56} RbH,⁵⁷ and CsH.⁵⁸ Its application in the present work on the LiCs molecule can be considered as the first application for a neutral heteronuclear pair of alkali diatomic systems. This diabatisation method can be considered as among the most effective for molecular ab initio calculations as shown in ref 59. We briefly give the outlines of the method based on variational Effective Hamiltonian theory⁶⁰ and an effective metric.⁵³ The idea is to estimate the nonadiabatic coupling between the considered adiabatic states and to cancel it by an appropriate unitary transformation. This unitary transformation matrix, U , will provide us with the quasi-adiabatic energies and wave functions. The quasi-adiabatic wave functions are therefore written as a linear combination of the adiabatic ones. This non adiabatic coupling estimation is closely related to an overlap matrix between the R-dependent adiabatic multiconfigurational states and the reference states corresponding to a fixed large distance states. The quasi-adiabatic states result from the symmetrical orthonormalization of the projection of the model space wave functions (references) onto the selected adiabatic wave functions (target space). The overlap

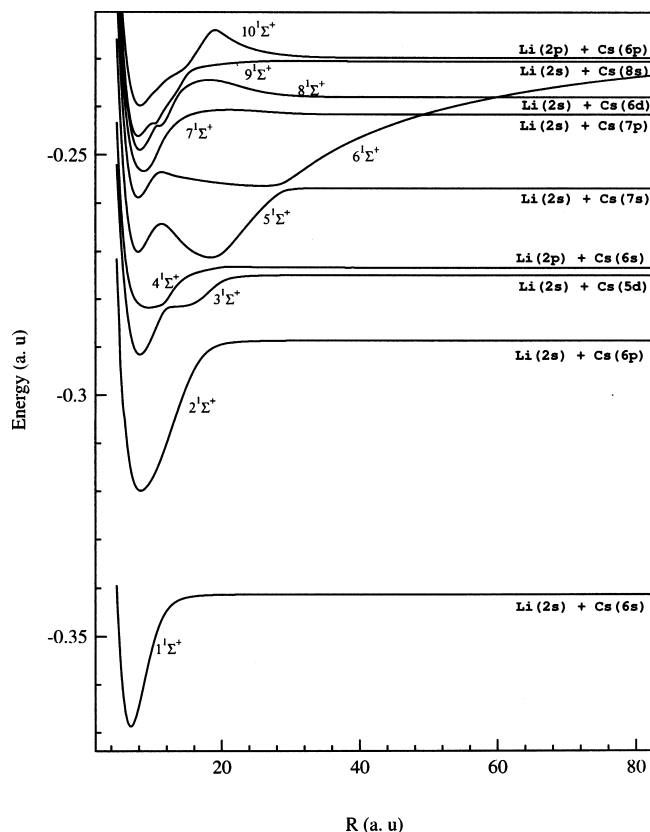


Figure 1. Potential energy curves for the 10 lowest $1\Sigma^+$ states of LiCs.

matrix involved in the projection is obviously an overlap matrix over nonorthogonal functions since the two sets are related to different interatomic distances. The diabatisation method based on effective Hamiltonian theory uses reference states usually taken at infinite distance corresponding to the dissociation limit. In our study the reference states correspond to the adiabatic ones taken at large and fixed distance. At this distance the adiabatic and diabatic states coincide. In our work this large and fixed distance is 150 au, for which all adiabatic states have reached their asymptotic limits. We take the origin on the heavier atom, which corresponds here to the Cesium atom. This diabatisation scheme is based on the overlap matrix between the reference states and the adiabatic ones that correspond to a crude numerical estimation of the nonadiabatic coupling, but do not involve the electric dipole matrix at all.

III. Results and Discussion

III.1. Adiabatic Potential Energy and Spectroscopic Constants. We have determined the adiabatic potential energy curves of about 38 electronic states of $1,3\Sigma^+$, $1,3\Pi$, and $1,3\Delta$ symmetries for the LiCs molecule dissociating into Cs (6s, 6p, 5d, 7s, 7p, 6d, 8s) + Li (2s, 2p, 3s). The potential energy has been calculated for a large and dense grid of intermolecular distance from 5.9 to 150 au. The $1\Sigma^+$ and $3\Sigma^+$ electronic states are displayed, respectively, in Figures 1 and 2, whereas the $1,3\Pi$ and $1,3\Delta$ states are displayed, respectively, in Figures 3 and 4. An important general behavior can be observed for the higher excited states. It corresponds to the existence of undulations, which often lead to double and some times to triple wells and barriers. Most of them are not due to the avoided crossings but to the undulating atomic Rydberg orbitals. They are related to a closed shell ion passing through antinodes in the Rydberg wave function of the other atom. We also observe many avoided

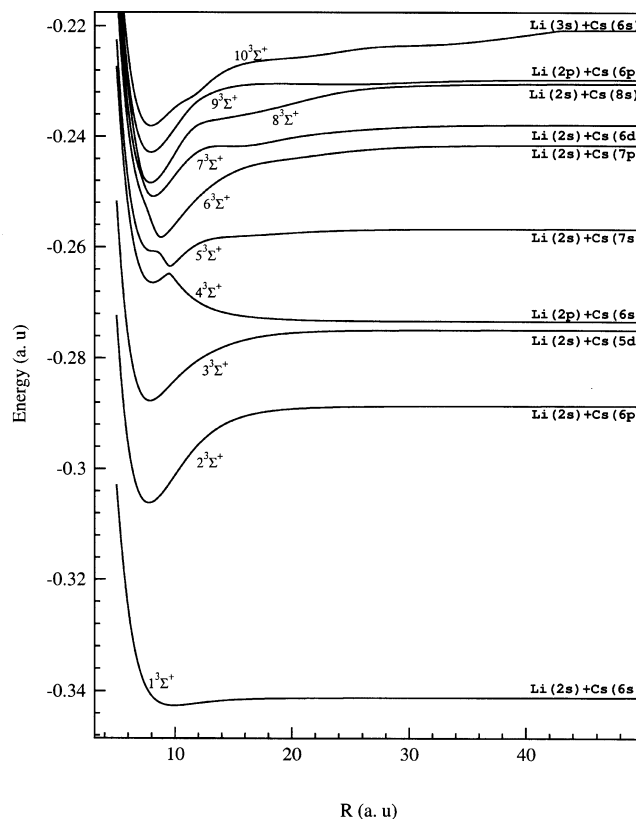


Figure 2. Potential energy curves for the 10 lowest $3\Sigma^+$ states of LiCs.

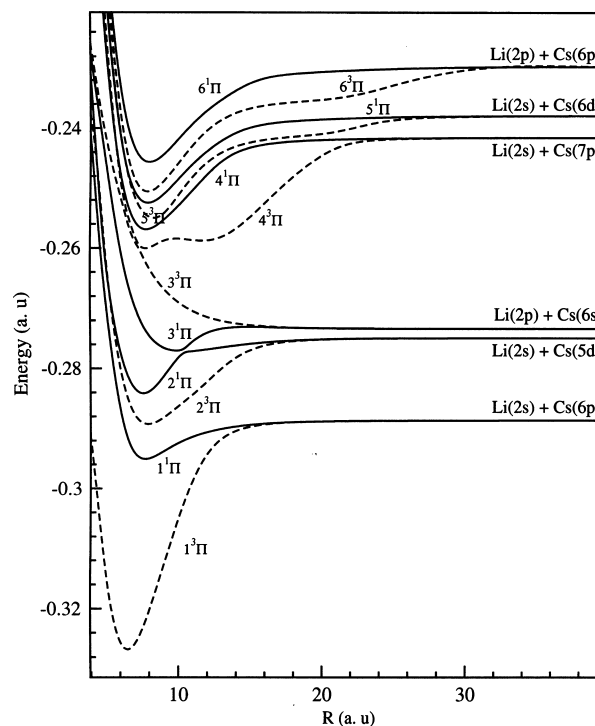


Figure 3. LiCs adiabatic potential energy curves for the 1Π (solid lines) and the 3Π (dashed lines).

crossings, which can be explained by the interaction with the ionic states Cs^+Li^- and Cs^-Li^+ . For almost all these curves we have extracted the spectroscopic constants (R_e , D_e , T_e , ω_e , $\omega_e x_e$, and B_e), which are presented in Table 3 and compared with the available theoretical studies.^{21,28,29,31} A rather good agreement is observed between our spectroscopic constants and the

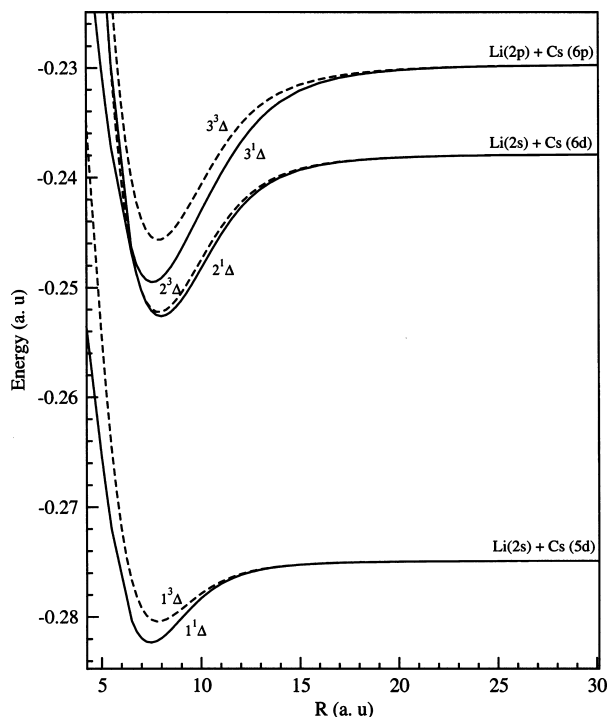


Figure 4. LiCs adiabatic potential energy curves for the 1Δ (solid lines) and the 3Δ (dashed lines).

TABLE 3: Spectroscopic Constants of the $1\Sigma^+$ States of LiCs Molecule

state	R_e (Å)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	ref
$1^1\Sigma^+(X)$	3.609	6032		186.84	0.63	0.1962	This work
	3.650	5807		183			CI ^a
	3.615			187.10		0.1935	CI ^b
	3.622	6067		186.52			CCSDT-SF ^c
	3.604	5783					CI ^d
		6108.9		168.822	0.5435	0.18187	PM ^e
	3.6681	5875.455					Expt. ^f
		5990 ± 170					Expt. ^g
$2^1\Sigma^+$	4.381	6865	10715	104.04	0.50	0.1333	This work
	4.378		10664	104.80		0.1320	CI ^b
$3^1\Sigma^+$	4.318	3659	16932	117.69	0.50	0.1372	This Work
	4.307		16865	118.50		0.1364	CI ^b
$4^1\Sigma^+$	5.006	1856	19081	44.57	0.66	0.1022	This Work
	4.986		18998	45.74		0.1020	CI ^b
$5^1\Sigma^+$							
1st min	4.180	2924	21647	133.06	1.35	0.1463	This Work
	4.180		21618	133.3		0.1448	CI ^b
2nd min	9.784	3168	21403				This Work
$6^1\Sigma^+$							
1st min	4.191	3773	24140	123.81	1.04	0.1456	This Work
	4.190		24119	124.30		0.1441	CI ^b
2nd min	13.64	3241					This Work
$7^1\Sigma^+$							
1st min	4.593	3387	25331	88.63	-0.34	0.1211	This Work
	4.561		25316	88.16		0.1215	CI ^b
2nd min	22.630	807	27911				This Work
3rd min	25.690	848	27870				This Work
$8^1\Sigma^+$							
1st min	4.302	4072	26283	125.91	0.99	0.1380	This Work
2nd min	31.083	1700	28655				This Work
$9^1\Sigma^+$	4.169	3604	26913	123.39	2.22	0.1469	This Work
$10^1\Sigma^+$							
1st min	4.333	2441	28309	109.52	90.69	0.2458	This Work
2nd min	24.696	234	30515				This Work

^a Reference 29. ^b Reference 21. ^c Reference 31. ^d Reference 28. ^e PM (perturbation method), ref 12. ^f Reference 33. ^g Reference 37.

theoretical existing works. For example, for the ground state, we found an equilibrium distance $R_e = 3.609$ Å, whereas Igel-Mann et al.,²⁹ Korek et al.,²¹ and Aymar et al.²⁸ found, respectively, 3.650, 3.615, and 3.604 Å. The same good

TABLE 4: Spectroscopic Constants of the $3\Sigma^+$ States of LiCs Molecule

state	R_e (Å)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	ref
$1^3\Sigma^+(a)$	5.233	308	5725	41.42	1.62	0.0934	This Work
	5.2472	309					Expt. ^a
	5.229	307					CI ^b
$2^3\Sigma^+$	4.106	3851	13730	124.64	1.12	0.1515	This Work
	4.104		13682	126.60		0.1502	CI ^b
$3^3\Sigma^+$	4.159	2812	17779	117.94	1.59	0.1479	This Work
	4.175		17712	116.50		0.1451	CI ^b
$4^3\Sigma^+$	4.270	-1530	22467	112.99	1.17	0.1402	This Work
	4.274	-1545	22451	112.60		0.1385	CI ^b
$5^3\Sigma^+$	5.059	1472	23099	217.23	19.64	0.0999	This Work
$6^3\Sigma^+$	4.646	3676	24237	180.41	8.72	0.1183	This Work
$7^3\Sigma^+$							
1st min	4.302	2849	25869	136.68	2.01	0.1382	This Work
	4.272		25809	146.90		0.1388	CI ^b
2nd min	7.980	859					This Work
$8^3\Sigma^+$	4.175	3945	26410	134.29	0.71	0.1468	This Work
$9^3\Sigma^+$							
1st min	4.196	2894	27623	123.38	1.19	0.1450	This Work
2nd min	12.859	187					This Work
$10^3\Sigma^+$	4.196	3813	28671	118.81	1.56	0.1452	This Work

^a Reference 33. ^b Reference 21.

agreement is observed between our other spectroscopic constants ($D_e = 6032$ cm^{-1} , $\omega_e = 186.84$ cm^{-1} and $B_e = 0.1962$ cm^{-1}) and those found by Korek et al.²¹ ($D_e = 5996$ cm^{-1} , $\omega_e = 187.10$ cm^{-1} , $B_e = 0.1935$ cm^{-1}). However, the well depth of Igel-Mann et al.²⁹ for the ground state is underestimated ($D_e = 5783$ cm^{-1}). Recent theoretical CC calculations have been performed by Fleig and Sørensen³ to test and apply a relativistic 4-component multi-reference CC method on the ground state of LiCs. Their best spectroscopic constants, are $R_e = 3.622$ Å, $D_e = 6067$ cm^{-1} , and $\omega_e = 186.52$ cm^{-1} , in very good agreement with our values, compared to other theoretical works.^{21,28,29,31} Recently Staunum et al.³³ have investigated the ground state of the LiCs and they have found $R_e = 3.6681$ Å and $D_e = 5875.445$ cm^{-1} , which are also in good agreement with our results. The $2^1\Sigma^+$, $3^1\Sigma^+$, and $4^1\Sigma^+$ excited states exhibit potential well depths of, respectively, 6865, 3659, and 1856 cm^{-1} located at 4.381, 4.318, and 5.006 Å, which are in good agreement with those found by Korek et al.²¹ In contrast, the higher $5-10^1\Sigma^+$ states exhibit double potential wells and some time triple wells as in the case of the $7^1\Sigma^+$ state. Korek et al.²¹ in their work presented only the first minimum, as they have performed their calculation for a reduced grid. The same good agreement is observed between our work and that of Korek et al.²¹ for the $2-7^1\Sigma^+$ excited states, which is not surprising as we use similar pseudopotential methods. The $8-10^1\Sigma^+$ higher excited states are studied here for the first time.

Table 4 presents the spectroscopic constants of the $1-10^3\Sigma^+$ states. The $1^3\Sigma^+$ state has been experimentally explored recently by Staunum et al.³³ It exhibits a very small potential well of 308 cm^{-1} located at an equilibrium distance of 5.233 Å, compared with the experimental values of Staunum et al.³³ ($R_e = 5.2472$ Å and $D_e = 309$ cm^{-1}) and the theoretical work of Korek et al. ($R_e = 5.229$ Å and $D_e = 307$ cm^{-1}). As we can see from this table, our equilibrium distance is in better agreement with the experimental values than that given by Korek et al.²¹ The spectroscopic constants of the $1^3\Pi$ and $1^3\Delta$ states are presented in Table 5. All of them are attractive and exhibit well depths of some thousands of cm^{-1} located at distances close to the equilibrium distance of the LiCs^+ ionic molecule ($R_e = 4.30$ Å⁴³). For all these states of different symmetries, many avoided crossings have been located at large distance as well as at short distance. Their existences will generate large non-

TABLE 5: Spectroscopic Constants of the $1^3\Pi$ and $1^3\Delta$ States of LiCs Molecule

state	R_e (Å)	D_e (cm $^{-1}$)	T_e (cm $^{-1}$)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)	B_e (cm $^{-1}$)	ref
$1^1\Pi$ (B)	4.080	1415	16165	106.35	2.35	0.1535	This work
	4.104		15133	106.00		0.1513	CI ^a
	4.12178	1595.495	16012.217				Expt. ^b
$2^1\Pi$ (D)	4.016	2021	18570	126.68	0.76	0.1582	This Work
	4.008		18542	128.60		0.1575	CI ^a
	4.055	2178.93	18293.37				Expt. ^b
$3^1\Pi$	5.244	813	20123	94.78	12.22	0.0932	This Work
	4.089		20095	94.55		0.0919	CI ^a
	4.113	3367	24546	116.05	1.36	0.1506	This Work
$4^1\Pi$	4.113		24517	115.70		0.1495	CI ^a
	4.185	3197	25521	116.19	1.01	0.1458	This Work
	4.421		25512	116.10		0.1438	CI ^a
$5^1\Pi$	4.233	3493	27024	116.190	1.01	0.1425	This Work
	4.080	1415	16165	106.35	2.35	0.1535	This Work
	4.104		16133	106.00		0.1513	CI ^a
$2^3\Pi$	4.016	2021	18570	126.68	0.76	0.1582	This Work
	4.008		18542	128.60		0.1575	CI ^a
	5.244	813	20123	94.78	12.22	0.0932	This Work
$3^3\Pi$	4.089		20095	94.55		0.0919	CI ^a
	4.116	3367	24546	116.05	1.36	0.1506	This Work
	4.113		24517	115.70		0.1495	CI ^a
$5^3\Pi$	4.185	3197	25521	116.19	1.01	0.1458	This Work
	4.421		25512	116.10		0.1438	CI ^a
	4.174	4584	25933	127.24	1.03	0.1464	This Work
$6^3\Pi$	4.420		26045	127.60		0.1421	CI ^a
	3.942	1628	18963	114.33	1.47	0.1646	This Work
	3.964		19036	111.00		0.1610	CI ^a
$1^1\Delta$	4.233	3232	25486	120.43	0.68	0.1427	This Work
	4.226		25698	113.90		0.1418	CI ^a
	4.000	4352	26164	128.88	0.81	0.1595	This Work
$3^1\Delta$	3.965		26584	115.00		0.1604	CI ^a
	4.132	1209	19381	102.64	1.84	0.1495	This Work
	4.165		19430	99.35		0.1458	CI ^a
$2^3\Delta$	4.180	3153	25565	124.78	0.89	0.1495	This Work
	3.566		26950	299.20		0.1989	CI ^a
	4.159	3513	27003	28.43	0.99	0.1477	This Work
$3^3\Delta$	4.087		28216	192.50		0.1513	CI ^a

^a Reference 21. ^b Reference 36.

adiabatic coupling and lead to an undulating behavior of the higher excited states at large internuclear distances. Very recently, Stein et al.³⁶ have studied the $1^1\Pi$ (B) and $2^1\Pi$ (D) excited states using the fourier-transform spectroscopy. They found for the $1^1\Pi$ (B) and $2^1\Pi$ (D) states potential well depths of, respectively, 1595.495 and 2178 cm $^{-1}$ located at an equilibrium distance of, respectively, 4.12178 and 4.055 Å. Our

equilibrium distances are in good agreement with these data, in contrast to our D_e values, which seem to be underestimated by more than 150 cm $^{-1}$ for both states. The same observation is seen between the theoretical values found by Korek et al.²¹ and the experimental ones³⁶ for these states. Our transition energies (T_e) for the $1^1\Pi$ (B) and $2^1\Pi$ (D) states are overestimated compared to the experimental ones (see Table 5) by, respectively, 152.73 and 276.63 cm $^{-1}$. This can not be attributed to the dissociation limits as our Li(2s) + Cs(6p) and Li(2s) + Cs(5d) atomic energy limits differ only by 0.1 and 0.2 cm $^{-1}$ from the experimental ones. However, this can be explained by the difference between our well depths and the experimental ones for the two states and the basis set accuracy limitation.

III.2. Quasi-Adiabatic Potential Energy Curves. Figure 5 presents the quasi-adiabatic potential energy curves related to the $1-10^1\Sigma^+$ adiabatic ones and named D_{1-10} . We clearly observe that the first quasi-adiabatic curve called D_1 , dissociating into Li $^-$ Cs $^+$, crosses all the other D_{2-10} states at different distances. The lowest crossings in energy occur with the quasi-adiabatic state Li(2s) + Cs(6s) around 11.38 au and with the Li(2s) + Cs(6p) state around 16.68 au. The other crossings occur at much larger distances and higher energies. The real crossings in the diabatic representation are transformed into avoided crossings in the adiabatic one. The ionic curve D_1 (Li $^-$ Cs $^+$) nicely behaves as $1/R$ at large internuclear distances. The other ionic state associated to the Cs $^-$ Li $^+$ ionic character is expected to cross the neutral excited states at shorter distances than D_1 . However this second ionic state is not here fully described and followed up to dissociation, because of the huge number of states needed. Therefore, we have actually only some imprint with the second series of crossings involving D_{10} at short distances.

Figures 6–10 present, respectively, the quasi-adiabatic potential energy curves for the $1-10^3\Sigma^+$, $1-6^1\Pi$, $1-6^3\Pi$, $1-3^1\Delta$, and $1-3^3\Delta$ states. We observe various crossings and undulations with repulsive barriers at short distances. Interestingly, these barriers are similar to the ones found for the corresponding singlet states. For example the quasi-adiabatic states D_2 , D_3 , and D_4 present barriers decreasingly large and at larger distances, both in triplet and singlet symmetries. This effect was related in previous studies with the Fermi model,⁶¹ where an atom is colliding with a Rydberg electron, and the potential is then proportional to the scattering length and to the Rydberg

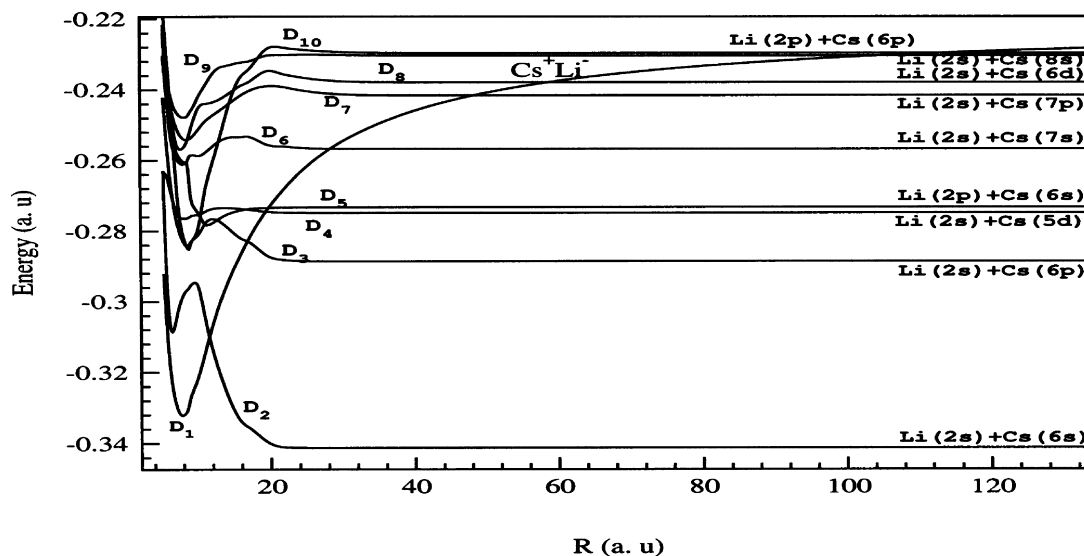


Figure 5. Quasi-Adiabatic potential energy curves for the 10 lowest $1^1\Sigma^+$ states of LiCs.

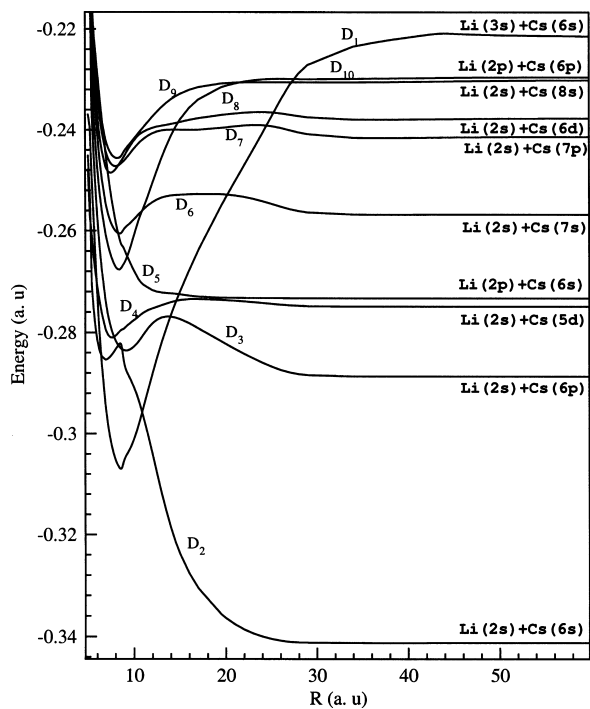


Figure 6. Quasi-diabatic potential energy curves for the 10 lowest $^3\Sigma^+$ states of LiCs.

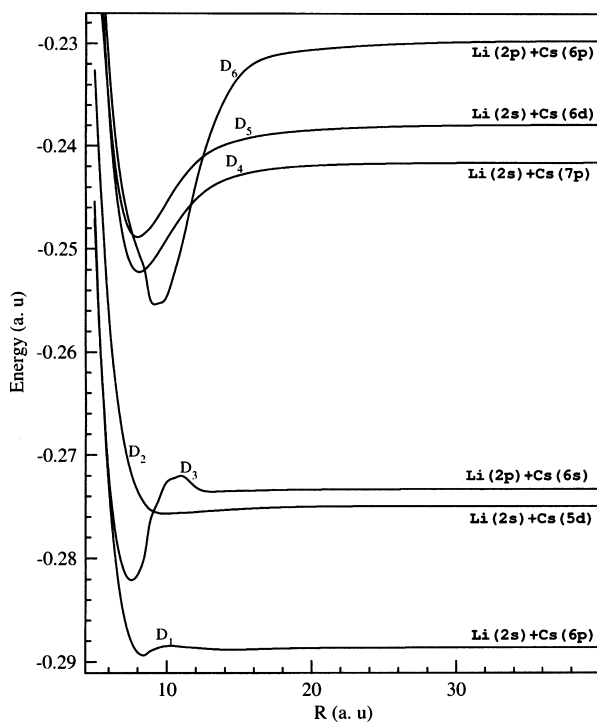


Figure 7. Quasi-diabatic potential energy curves for the six lowest $^1\Pi$ states of LiCs.

amplitude. For D_2 , D_3 , and D_4 , Rydberg wave functions of Cs involving, respectively, 6s, 6p, and 5d, and the Li atom in its ground state (2s), and the quasi-diabatic potentials simply reflect the amplitude of these Rydberg states. However, this qualitative analysis is difficult to pursue further because there are also interactions between the quasi-diabatic states, and when both atoms are in Rydberg states the Fermi model cannot be easily applied. The modulations in the Rydberg curves were predicted by Greene et al.⁶² to hold bound ultracold and ultralong range molecular states, and some of these states were recently observed in an ultracold gas of Rb atoms.⁶³

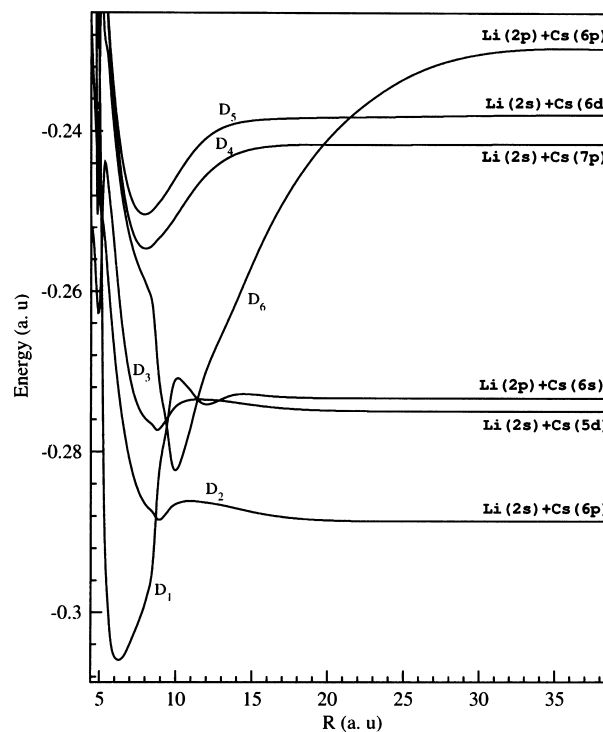


Figure 8. Quasi-diabatic potential energy curves for the six lowest $^3\Pi$ states of LiCs.

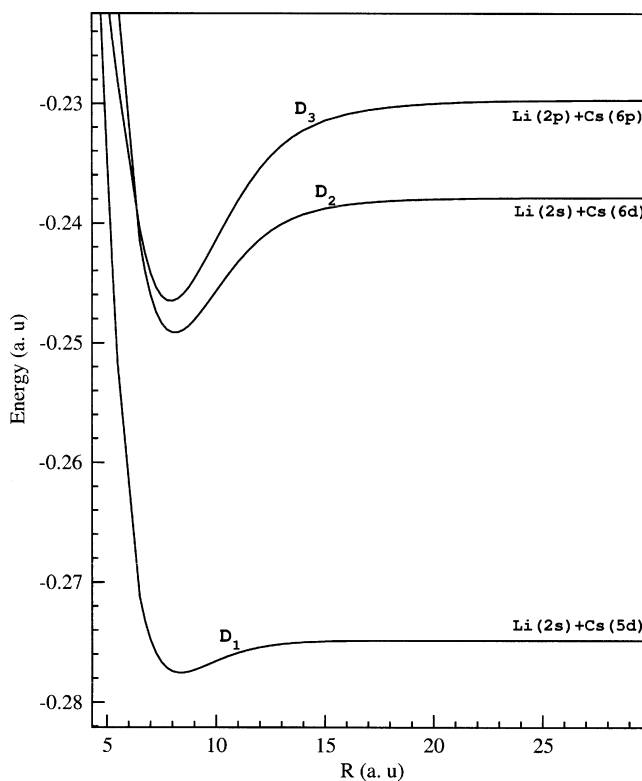


Figure 9. Quasi-diabatic potential energy curves for the three lowest $^1\Delta$ states of LiCs.

III.3. Permanent and Transition Dipole Moments. The knowledge of accurate electronic properties is necessary for obtaining ultracold dipolar heteronuclear alkali molecules. Furthermore, their dipole moment can be considered as a sensitive test for the accuracy of the calculated electronic wave functions and energies. For this aim, we have determined the adiabatic and the quasi-diabatic permanent dipole moments for

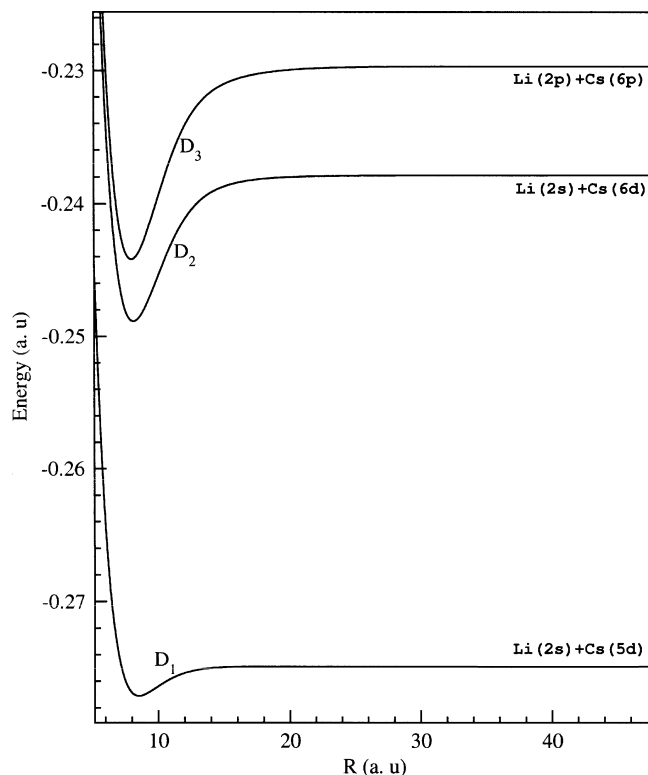


Figure 10. Quasi-diatomic potential energy curves for the three lowest $^3\Delta$ states of LiCs.

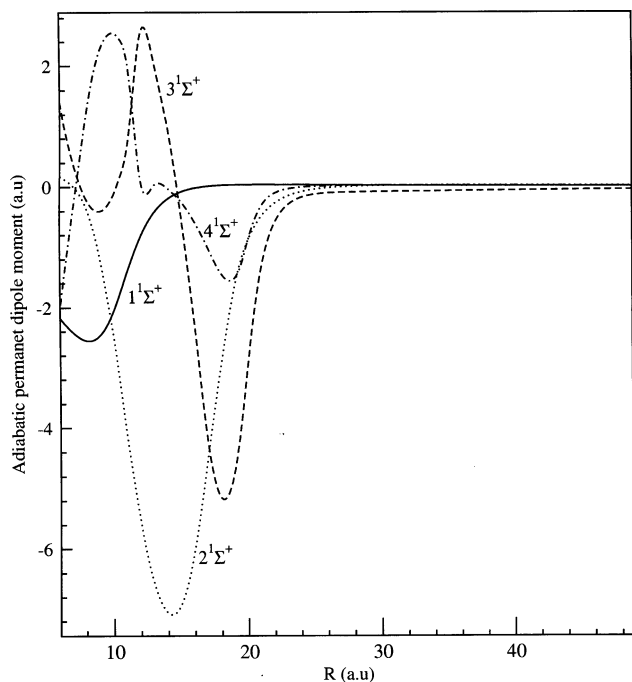


Figure 11. Adiabatic permanent dipole moment of the first four $^1\Sigma^+$ states of LiCs.

the large and dense grid of internuclear distances, from 5.9 to 150 au. To understand the ionic behavior of the excited electronic states, we have presented the adiabatic permanent dipole moment of the $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ symmetries states function of the internuclear distance: R . Figure 11 presents the adiabatic permanent dipole moment of the four first states of $^1\Sigma^+$ symmetry. We remark that the dipole moment of 1 and 2 $^1\Sigma^+$ states is significant, especially, in the region of their Li^-Cs^+ ionic character. The same observation is seen for the $3^1\Sigma^+$ and

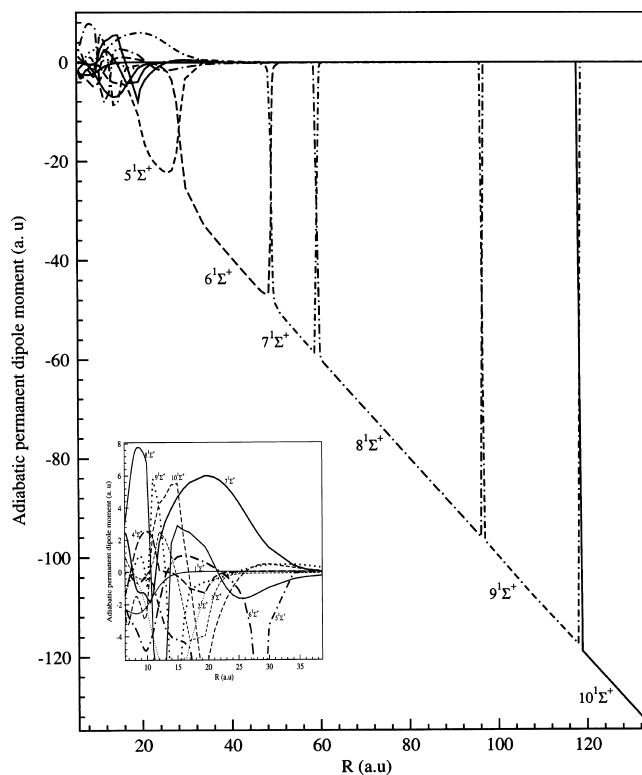


Figure 12. Adiabatic permanent dipole moment of the 5–10 $^1\Sigma^+$ states of LiCs.

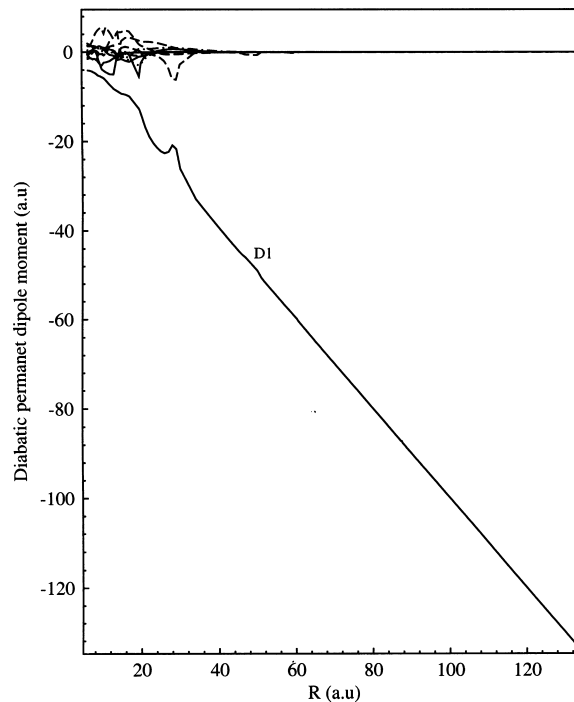


Figure 13. Quasi-diatomic permanent dipole moment of the first 10 $^1\Sigma^+$ states of LiCs.

$4^1\Sigma^+$ states but with a double ionic character related to Li^+Cs^- at short distance and to Li^-Cs^+ at larger distance. They exhibit positive and negative dipole moment. However, the permanent dipole moment of these 1–4 $^1\Sigma^+$ states does not behave as a pure linear function of R . Figure 12 displayed the permanent dipole moment as a function of R , the interatomic distance, for the remaining 5–10 $^1\Sigma^+$ states. We remark that the dipole moment of these states, one after another, behaves as a linear function

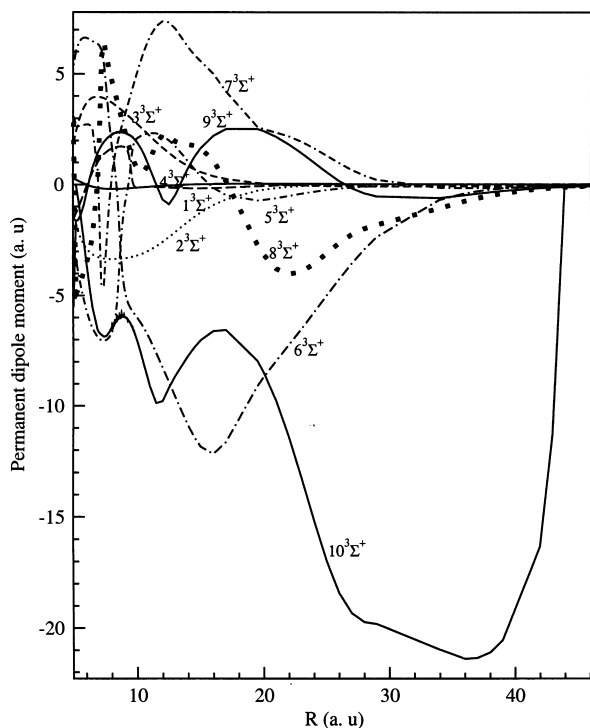


Figure 14. Adiabatic permanent dipole moment of the first 10 $^3\Sigma^+$ states of LiCs.

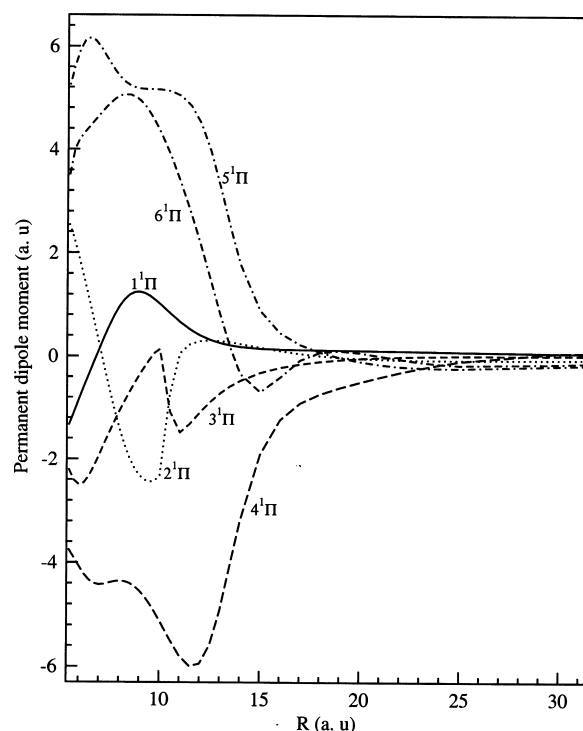


Figure 15. Adiabatic permanent dipole moment of the first six $^1\Pi$ states of LiCs.

of R and then drops to zero at particular distances corresponding to the avoided crossings between the two neighbor electronic states. If these curves are combined, they produce piecewise the whole $-R$ function due to the ionic character of these states. The discontinuities between the consecutive parts are due to the avoided crossings, and such nodes will disappear in the diabatic representation and will lead to a full linear curve corresponding to the dipole moment of the pure ionic state as it was observed previously in the LiH, RbH, and CsH

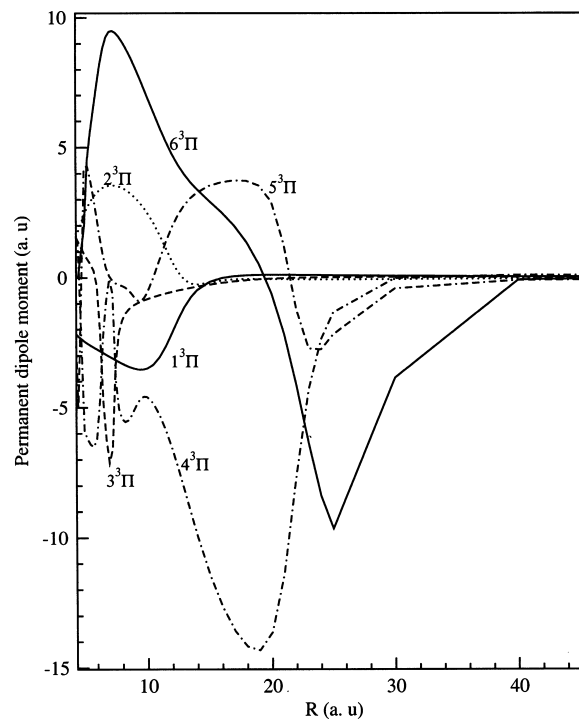


Figure 16. Adiabatic permanent dipole moment of the first six $^3\Pi$ states of LiCs.

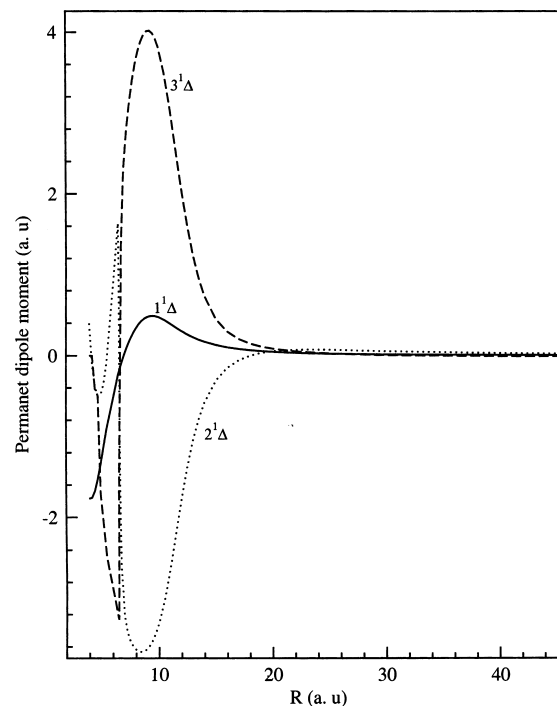


Figure 17. Adiabatic permanent dipole moment of the first three $^1\Delta$ states of LiCs.

molecules.^{56–58} This observation is well illustrated by Figure 13, which presents the quasi-diabatic permanent dipole moment of the first 10 $^1\Sigma^+$ states, which are obtained by simple rotation of the adiabatic dipole moment matrix. In the diabatic representation such nodes disappear and lead to a full linear curve corresponding to the dipole moment of the pure ionic state as it was observed previously in the LiH,⁵⁶ RbH,⁵⁷ and CsH⁵⁸ molecules. The distance when the two dipole moments of neighbor states are the same corresponds to the avoided crossing between them. For a better description, the dipole moment was

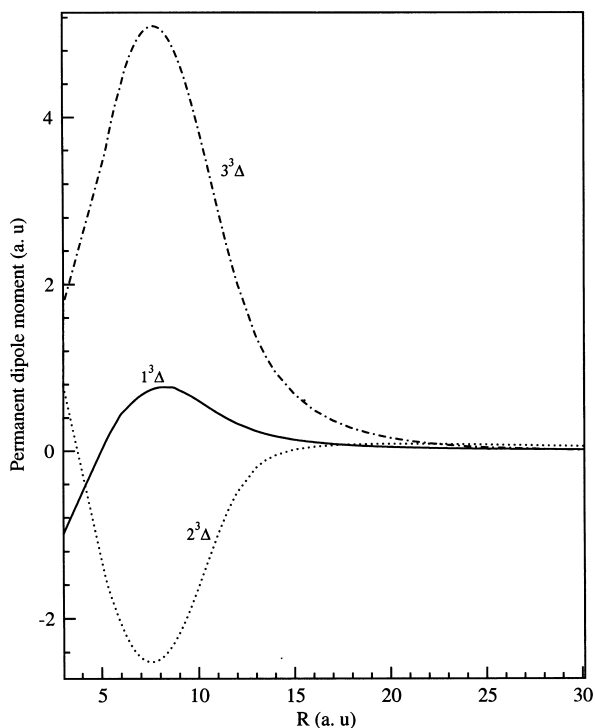


Figure 18. Adiabatic permanent dipole moment of the first three 3Δ states of LiCs.

determined for a large number of internuclear distances especially around the avoided crossing positions. The difference between two successive points in this region is 0.01 au. This proves the ionic structure and the long-range polar character of such excited states. Compare this to LiH,⁵⁶ where this linear behavior has started with the first $1^1\Sigma^+$ state, the ground state $X^1\Sigma^+$, since the LiH system is polar and its ground state presents significant permanent dipole moment. Clear ionic behaviors appear here only for the excited states since the ground state is much less polar than for LiH. We note that the second ionic curve does not appear clearly either in the adiabatic and or in the diabatic representations. We observe that some states, such as the $7-10^1\Sigma^+$ states, have also positive permanent dipole moment at short and intermediate distance in addition to the negative one at larger distances, which could be relative to the other ionic state Cs^-Li^+ . Therefore, here we have two ionic diabatic states. The first one is $D_1 (\text{Li}^-\text{Cs}^+)$ and as can be seen in Figure 13, its permanent dipole moment nicely behaves as $-R$, as expected, although there is some numerical noise around some avoided crossings. The second one is the Cs^-Li^+ state and should present a permanent dipole moment of opposite sign, which is positive. The permanent dipole moment of the ground state $X^1\Sigma^+$ at its equilibrium distance is compared with previous theoretical and experimental works. Our value of 6.05 D agrees well the experimental value⁶⁴ of 6.30 D and is in better agreement than the available theoretical values of Aymar et al.²⁸ and Korek et al.²¹ of, respectively, 5.52 and 5.48 D. The permanent dipole moment at the equilibrium distance for the excited states can be derived from our data provided as Supporting Information.

The permanent dipole moment has been also determined for the electronic states of the $3\Sigma^+$, 1Π , 3Π , 1Δ , and 3Δ remaining symmetries. Their permanent dipole moments are displayed in Figures 14–18. As it is expected, such quantity is not negligible for these states and it becomes more significant for higher excited states. In particular, Figure 18 shows the permanent dipole moment for the three (1Δ and 3Δ) studied states. For

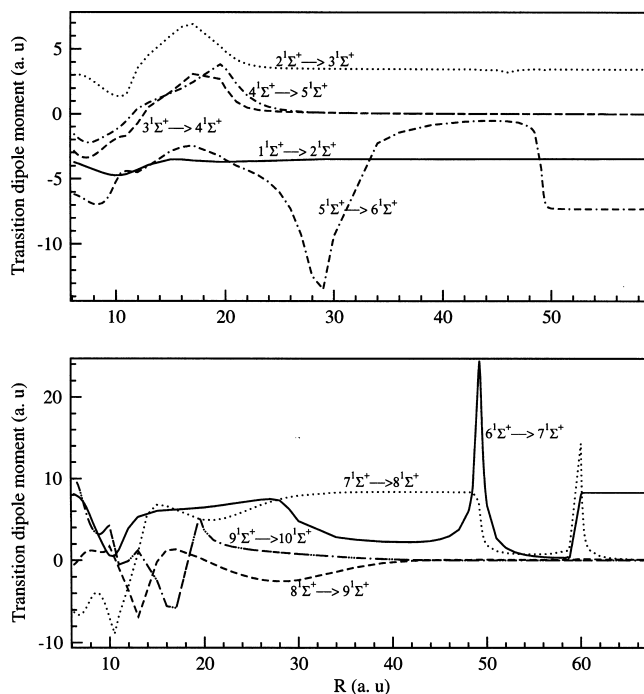


Figure 19. Transition dipole moment between neighbor states of $1\Sigma^+$ symmetry.

example, we remark a significant dipole moment in a particular region and then it vanishes rapidly to zero. The region located at intermediate distance corresponds to the repulsive part of their deep potential wells.

For a better understanding of the role of the avoided crossings, we have determined the transition dipole moment between neighbor $1\Sigma^+$, $3\Sigma^+$, 1Π , 3Π , 1Δ , and 3Δ adiabatic states. They are displayed in Figures 19–23. We observe many peaks located at particular distances very close to the avoided crossings position in adiabatic representation. Their positions are reported in Table 6.

IV. Conclusion

In this paper, we have performed an ab initio study for nearly 38 electronic states of the LiCs molecule dissociating into Cs

TABLE 6: Avoided Crossing Positions

states	position (au)
$3^1\Sigma^+/4^1\Sigma^+$	11.84
$4^1\Sigma^+/5^1\Sigma^+$	18.95
$5^1\Sigma^+/6^1\Sigma^+$	28.89
$6^1\Sigma^+/7^1\Sigma^+$	9.78
	49.16
$7^1\Sigma^+/8^1\Sigma^+$	59.88
$8^1\Sigma^+/9^1\Sigma^+$	10.55
	13.65
	107.66
$9^1\Sigma^+/10^1\Sigma^+$	15.08
	113.21
$4^3\Sigma^+/5^3\Sigma^+$	9.52
$7^3\Sigma^+/8^3\Sigma^+$	7.20
$8^3\Sigma^+/9^3\Sigma^+$	6.20
	11
	29
$9^3\Sigma^+/10^3\Sigma^+$	12
$2^1\Pi/3^1\Pi$	10.41
$3^3\Pi/4^3\Pi$	7.23
$5^3\Pi/6^3\Pi$	5.01
$2^1\Delta/3^1\Delta$	6.33

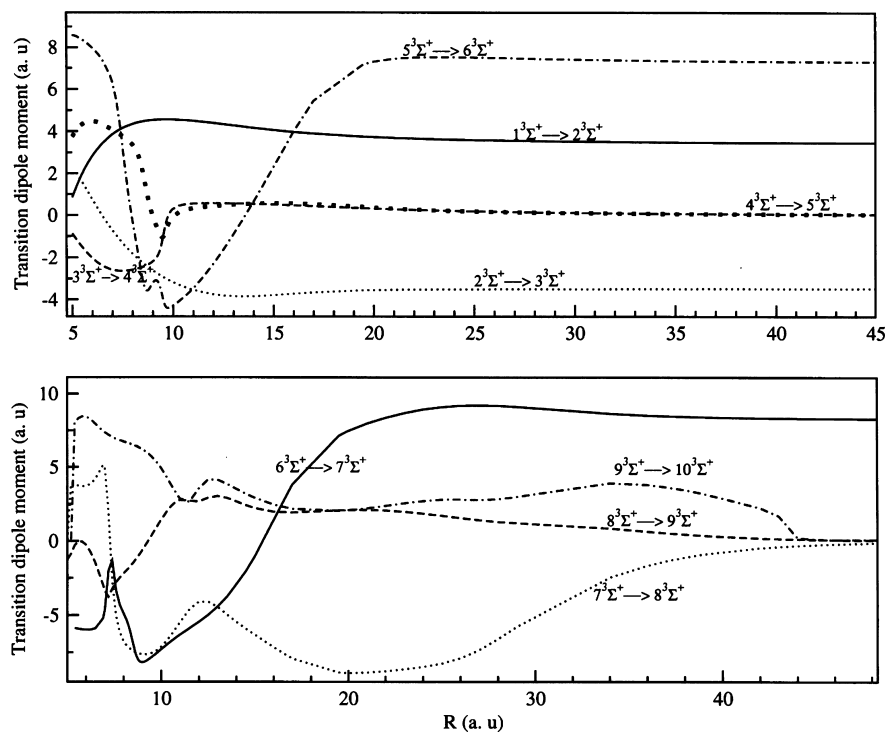


Figure 20. Transition dipole moment between neighbor states of $3\Sigma^+$ symmetry.

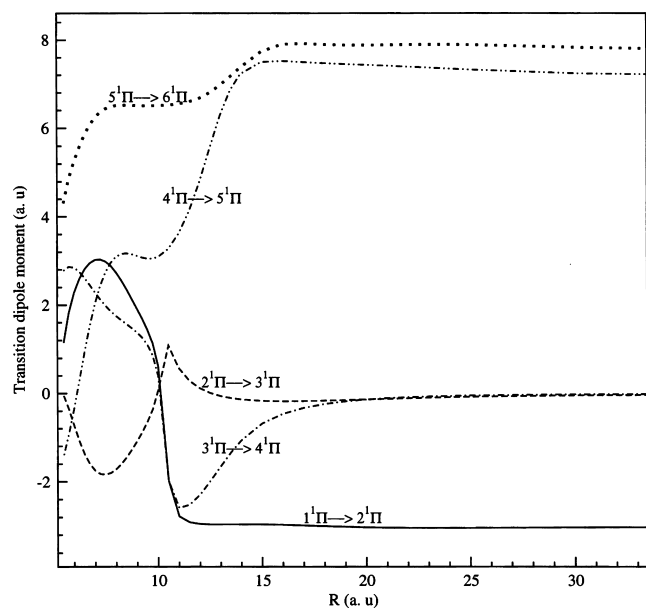


Figure 21. Transition dipole moment between neighbor states of 1Π symmetry.

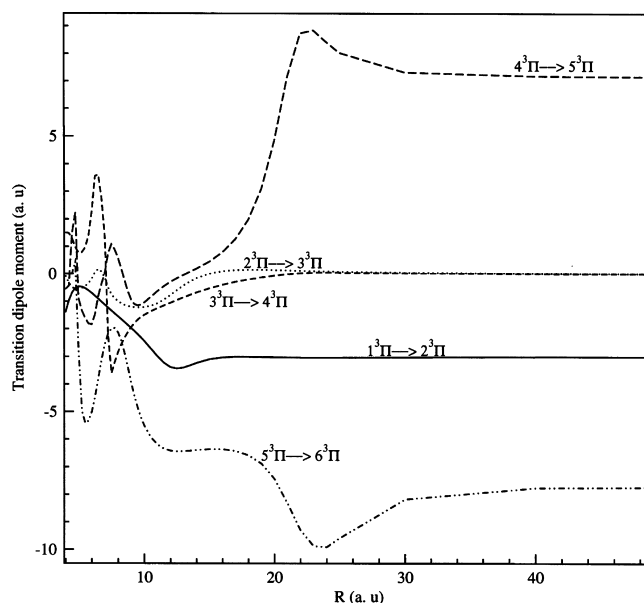


Figure 22. Transition dipole moment between neighbor states of 3Π symmetry.

(6s, 6p, 5d, 7s, 7p, 6d, 8s) and Li (2s, 2p, 3s). We have used nonempirical pseudopotentials, parametrized l-dependent core polarization potentials, and full valence CI calculations. The adiabatic potential energy curves and permanent and transition dipole moments have been performed for a large and dense grid of internuclear distances varying from 5.9 to 150 au. The spectroscopic constants of the $1-10^{1,3}\Sigma^+$, $1-6^{1,3}\Pi$, and $1-3^{1,3}\Delta$ electronic states have been extracted and compared with the available theoretical^{12,21,28,29,31} and experimental works.^{33,36,37} A very good agreement is observed between our results and those of Korek et al. for the ground state $X^1\Sigma^+$ as well as with the experimental study of Stannum et al.³³ Our results for the $1^1\Pi$ (B) and $2^1\Pi$ (D) excited states were also compared with the

very recent experimental work of Stein et al.³⁶ and have shown a good agreement for the equilibrium distance. However, our well depths for both states are underestimated by more than 150 cm^{-1} compared to the experimental ones. The same remark can be concluded between the theoretical work of Korek et al.²¹ and the experimental study.

A diabatisation is performed for the first time to the LiCs molecule in order to determine the quasi-diabatic states. Their feature has revealed imprint of the two ionic states Li^-Cs^+ and Li^+Cs^- . The diabatic Li^-Cs^+ curve is observed to cross almost all of quasineutral states, leading in $1\Sigma^+$ symmetry to series of avoiding crossings located at short, intermediate, and large distances. Such crossings became avoided crossings in the

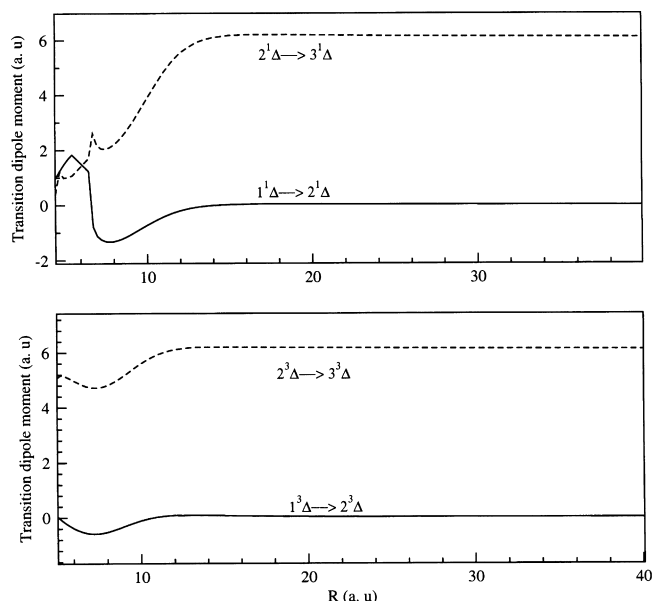


Figure 23. Transition dipole moment between neighbor states of 1Δ and 3Δ symmetries.

adiabatic scheme and gave undulating behaviors for several adiabatic states. These diabatic data will be used to determine accurate positions and nonradiative lifetimes of the vibrational levels belonging to the lower adiabatic LiCs states through a diabatic close coupling calculations.

For a better understanding of the ionic character of the electronic states of this molecule, we have performed calculations of the permanent dipole moment and the transition dipole moment between neighbor states. As it is expected the permanent dipole moment of the quasi-diabatic ionic state has shown an almost linear feature, especially for the higher excited states and at intermediate and large distances. The permanent dipole moment of the $1-4^1\Sigma^+$ states is found to be not significant, in contrast to that of the higher remaining $5-10^1\Sigma^+$ states. This behavior, as the function $-R$, leads to an important dipole moment corresponding to long-range ionic character, also in the adiabatic representation.

Higher excited states have shown undulations related to avoided crossings or undulating orbitals of the atomic Rydberg states. They have led to multiple potential barriers and wells in the potential energy curves. More attention and analysis for the spectacular undulating feature of the higher excited states could be performed using the multichannel quantum defect method.⁶⁵ Our accurate adiabatic potential energy and dipole moment data are made available as Supporting Information for such investigation and also for further theoretical and experimental uses.

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Supporting Information Available: The adiabatic potential energy curves, permanent and transition dipole moments of all studied states in this work are provided as support information

for further experimental and theoretical investigations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after ASAP Publication. This article posted ASAP on June 2, 2010. Figure 2 has been revised. The correct version posted on June 17, 2010.

References and Notes

- (1) Balakrishnan, N.; Dalgarno, A. *Chem. Phys. Lett.* **2001**, *341*, 652.
- (2) Bodo, E.; Gianturco, F. A.; Dalgarno, A. *J. Chem. Phys.* **2002**, *116*, 9222.
- (3) Rom, T.; Best, T.; Mandel, O.; Widera, A.; Greiner, M.; Hansch, T. W.; Bloch, I. *Phys. Rev. Lett.* **2004**, *93*, 073002.
- (4) Kajita, M. *Eur. Phys. J. D* **2003**, *23*, 337.
- (5) Krems, R. V. *Int. Rev. Phys. Chem.* **2005**, *24*, 99.
- (6) Avdeenkov, A. V.; Kajita, M.; Bohn, J. L. *Phys. Rev. A* **2006**, *73*, 022707.
- (7) Krems, R. V. *Phys. Rev. Lett.* **2006**, *96*, 123202.
- (8) Demille, D. *Phys. Rev. Lett.* **2002**, *88*, 067901.
- (9) Yelin, S. F.; Kirby, K.; Cote, R. *arXiv.org* **2006**, doi: quant-ph/0602030.
- (10) Kraemer, T.; Mark, M.; Walburger, P.; Danzl, J. G.; Chin, C.; Engesser, B.; Lange, A. D.; Pilch, K.; Jaakkola, A.; Nagerl, H. C.; Grimm, R. *Nature* **2006**, *440*, 315.
- (11) Kraft, S. D.; Staunum, P.; Lang, J.; Vogel, L. R.; Wester, R.; Weidemüller, M. *J. Phys. B: At. Mol. Opt. Phys.* **2006**, *39*, 5993.
- (12) Smirov, A. D. *J. Struct. Chem.* **2007**, *48*, 21.
- (13) Mabrouk, N.; Berriche, H.; Gadea, F. X. *AIP Conf. Proc.* **2007**, *963*, A, 23.
- (14) Mabrouk, N.; Zrafi, W.; Berriche, H.; Ben Ouada, H. *Lect. Ser. Comp. Comput. Sci.* **2006**, *7*, 1451.
- (15) Mabrouk, N.; Berriche, H. *J. Phys. B: At. Mol. Opt. Phys.* **2008**, *41*, 155101.
- (16) Mabrouk, N.; Berriche, H. *AIP Conf. Proc.* **2009**, in press.
- (17) Pavolini, D.; Gustavsson, T.; Spigelmann, F.; Daudey, J. P. *J. Phys. B: At. Mol. Opt. Phys.* **1989**, *22*, 1721.
- (18) Allouche, A. R.; Korek, M.; Fakhreddin, K.; Chalaan, A.; Dagher, M.; Taher, F.; Aubert-Frécon, M. *J. Phys. B: At. Mol. Opt. Phys.* **2000**, *33*, 2307.
- (19) Fahs, H.; Allouche, A. R.; Korek, M.; Aubert-Frécon, M. *J. Phys. B* **2002**, *35*, 1501.
- (20) Korek, M.; Allouche, A. R.; Kobeissi, M.; Chalaan, A.; Dagher, M.; Fakhreddin, F.; Aubert-Frécon, M. *Chem. Phys.* **2000**, *256*, 1.
- (21) Korek, M.; Allouche, A. R.; Fakhreddine, K.; Chalaan, A. *Can. J. Phys.* **2000**, *78*, 977.
- (22) Rousseau, S.; Allouche, A. R.; Aubert-Frécon, M. *J. Mol. Spectrosc.* **2000**, *203*, 235.
- (23) Rousseau, S.; Allouche, A. R.; Aubert-Frécon, M.; Magnier, S.; Kowalczyk, P.; Jastrzebski, W. *Chem. Phys.* **1999**, *247*, 193.
- (24) Magnier, S.; Aubert-Frécon, M.; Millié, P. *J. Mol. Spectrosc.* **2000**, *200*, 96.
- (25) Magnier, S.; Aubert-Frécon, M.; Millié, P. *Phys. Rev. A* **1996**, *54*, 204.
- (26) Schmidt-Mink, I.; Müller, M.; Meyer, W. *Chem. Phys. Lett.* **1984**, *112*, 120.
- (27) Petsalakis, I. D.; Tzeli, D.; Theodorakopoulos, G. *J. Chem. Phys.* **2008**, *129*, 054306.
- (28) Aymar, M.; Dulieu, O. *J. Chem. Phys.* **2005**, *122*, 204302.
- (29) Igel-Mann, G.; Wedig, U.; Fuentealba, P.; Stoll, H. *J. Chem. Phys.* **1986**, *84*, 5007.
- (30) Gonzalez-Ferez, R.; Mayle, M.; Schmelcher, P. *Chem. Phys.* **2006**, *329*, 203.
- (31) Fleig, T.; Sørensen, L. K. *John Neumann Inst. Comput. (NIC) Symp.* **2006**, *32*, 91.
- (32) Sørensen, L. K.; Fleig, T.; Olsen, J. J. *J. Phys. B: At. Mol. Opt. Phys.* **2009**, *42*, 165102.
- (33) Staunum, P.; Pashov, A.; Knockel, H.; Tieman, E. *Phys. Rev. A* **2007**, *75*, 042513.
- (34) Zanelatto, A. L. M.; Ribeiro, E. M. S.; Napolitano, R. D. J. *J. Chem. Phys.* **2005**, *123*, 014311.
- (35) Wang, H.; Stwalley, W. C. *J. Chem. Phys.* **1998**, *108*, 5767.
- (36) Stein, A.; Passhov, A.; Staunum, P. F.; Hnockel, H.; Tiemann, E. *Eur. Phys. J. D* **2008**, *48*, 177.
- (37) *Thermodynamic Properties of Individual Substances* [in Russian]; Nauka, Moscow, 1982; Vol. 4, Book 2.
- (38) Elkork, N.; Houalla, D.; Korek, M. *Can. J. Phys.* **2009**, *87*, 1079.
- (39) Durand, P.; Barthelat, J. *Chem. Phys. Lett.* **1974**, *27*, 191.
- (40) Barthelat, J. *Theor. Chim. Acta* **1975**, *38*, 283.
- (41) Berriche, H.; Gadea, F. X. *Chem. Phys.* **1995**, *191*, 119.

- (41) Berriche, H.; Tlili, C. *J. Mol. Struct.* **2004**, 682, 11.
- (42) Berriche, H. *J. Mol. Struct.* **2004**, 682, 89.
- (43) Ghanmi, C.; Bouzouita, H.; Berriche, H.; Ben Ouada, H. *J. Mol. Struct.* **2006**, 777, 81.
- (44) Berriche, H.; Ghanmi, C.; Ben Ouada, H. *J. Mol. Spectrosc.* **2005**, 230, 161.
- (45) Ghanmi, C.; Berriche, H.; Ben Ouada, H. *Comp. Mat. Scien.* **2007**, 38, 494.
- (46) Berriche, H. *J. Mol. Struct.* **2003**, 663, 101.
- (47) Müller, W.; Flesh, J.; Meyer, W. *J. Chem. Phys.* **1984**, 80, 3297.
- (48) Foucrault, M.; Millié, P.; Daudey, J. P. *J. Chem. Phys.* **1992**, 96, 1257.
- (49) Moore, C. E. , *Atomic Energy Levels, Natl. Bur. Stand. Circ. No. 467*; U.S GPO: Washington, DC, 1971.
- (50) Gadea, F. X.; Boutalib, A. *J. Phys. B* **1993**, 26, 61.
- (51) Boutalib, A.; Gadea, F. X. *J. Chem. Phys.* **1992**, 97, 1144.
- (52) Gadea, F. X. Thèse d'état, Théorie des Hamiltoniens effectifs, applications aux problèmes de diabatisation et de collision réactive, Université Paul Sabatier, Toulouse, France, 1987.
- (53) Gadea, F. X.; Pelissier, M. *J. Chem. Phys.* **1990**, 93, 545.
- (54) Berriche, H. Ph.D. Thesis, Etude spectroscopique ab-initio de LiH et LiH⁺ au delà de l'approximation de Born Oppenheimer, Paul Sabatier University, 1995.
- (55) Gadea, F. X.; Boutalib, A. *J. Phys. B* **1993**, 26, 61.
- (56) Berriche, H.; Gadea, F. X. *Chem. Phys. Lett.* **1995**, 247, 85.
- (57) Khelifi, N.; Zrafi, W.; Oujia, B.; Gadea, F. X. *Phys. Rev. A* **2002**, 65, 042513.
- (58) Zrafi, W.; Oujia, B.; Gadea, F. X. *J. Phys. B* **2006**, 39, 3815.
- (59) Romero, T.; Agular, A.; Gadea, F. X. *J. Chem. Phys.* **1991**, 110, 6219.
- (60) Gadea, F. X. *Phys. Rev. A* **1991**, 43, 1160.
- (61) Dickinson, A. S.; Gadea, F. X. *Phys. Rev. A* **2002**, 65, 052506.
- (62) Greene, C. H.; Dickinson, A. S.; Sadeghpour, H. R. *Phys. Rev. Lett.* **2000**, 85, 2458.
- (63) Bendkowsky, V.; Butscher, B.; Nipper, J.; Shaffer, J. P.; Löw, R.; Pfau, T. *Nature* **2009**, 458, 1005.
- (64) Tarnovsky, V.; Bunimovicz, M.; Vuskovic, L.; Stumpf, B.; Bederson, B. *J. Chem. Phys.* **1993**, 98, 3894.
- (65) Du, N. Y.; Greene, C. H. *Phys. Rev. A* **1987**, 36, 971.

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