Potential energy surfaces of the low-lying electronic states of the Li + LiCs system

P. Jasik[a,1], T. Kilich[a], J. Kozicki[b], J.E. Sienkiewicz[a,1]

[a]*Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gdańsk, Poland*
[b]*Faculty of Civil and Environmental Engineering, Gdańsk University of Technology, Gdańsk, Poland*

Abstract

Ab initio quantum chemistry calculations are performed for the mixed alkali triatomic system. Global minima of the ground and first excited doublet states of the trimer are found and Born-Oppenheimer potential energy surfaces of the Li atom interacting with the LiCs molecule were calculated for these states. The lithium atom is placed at various distances and bond angles from the lithium-caesium dimer. Three-body nonadditive forces of the Li_2Cs molecule in the global minimum are investigated. Dimer-atom interactions are found to be strongly attractive and may be important in the experiments, particularly involving cold alkali polar dimers.

Keywords: potential energy surfaces, Li2Cs, triatomic system, atom-molecule collisions, three-body nonadditive forces

PACS: 31.15.A-, 31.15.ae, 31.50.Bc, 31.50.Df, 33.15.Dj, 34.20.-b

1. Introduction

There is a growing demand for data concerning heteronuclear alkali-metal dimers interacting with an alkali-metal atom. The investigations are carried out in the three main streams: the electronic structure properties, the dissociation or fragmentation processes and the association processes. The very extensive

---

[1]Corresponding authors: patryk.jasik@pg.edu.pl (P. Jasik), jes@mif.pg.gda.pl (J.E. Sienkiewicz)

experimental and theoretical studies on the heteronuclear and homonuclear alkali trimers were given by the group of Ernst [1, 2, 3, 4, 5], where alkali quartet trimers formed on helium nanodroplets are probed by one-color femtosecond photoionization spectroscopy. The observation of predissociation in the mixed alkali trimer clusters was reported by the experimental group of Wöste [6]. The same group presented the coherent control of alkali cluster fragmentation dynamics [7]. The polar dimer gas can be controlled in optical traps and eventually converted into the quantum degenerate ultracold dipolar gas [8]. Triatomic systems attract considerable attention in the context of experiments involving cold and ultracold molecules [9]. Efficient control of such three-body interactions requires detailed knowledge of low-lying interatomic potentials. Among other data, the potential energy surfaces (PESs) for a dimer interacting with an atom are of growing interest since they may help to describe elastic and inelastic atom-molecule collisions [10, 11], particularly when experiments on magnetic tuning of Feshbach resonances [12, 13] and three-body recombination [14, 15] are considered.

In this paper, we study the interaction between the lithium atom and the lithium-caesium dimer. We also calculate the global minima of the ground $(1^2A')$ and first excited $(2^2A')$ doublet states of the Li_2Cs trimer, as well as three-body nonadditive contribution for the minimum of the ground state.

Until now, this system was very scarcely studied. To the authors' knowledge the first study concerning this system was performed in 1982 by Richtsmeier *et al.* [16], where energies of the optimized geometries for the linear LiCsLi in $D_{\infty h}$ and CsLiLi in $C_{\infty v}$ symmetries, as well as nonlinear Li_2Cs trimer in the C_{2v} symmetry were presented. This study was carried out by means of the diatomics-in-molecules (DIM) approximation and used empirically evaluated integrals. In turn, Żuchowski and Hutson [11] modeled the reactions involving pairs of the alkali metal dimers. Using the multireference average-quadratic coupled-cluster method (AQCC), they found the global minima of mixed alkali-metal trimers, including Li_2Cs.

2

2. Computational method

In our calculations, Li + LiCs is considered as an effective three-electron system. Each n-electron atom is replaced by one valence electron and the effective core consisting of a nuclei and n-1 electrons. Since our theoretical approach has
been already presented in a few earlier papers (e.g. [17, 18, 19, 20, 21]), here we give only salient details concerning pseudopotentials and atomic basis sets which differ from those used in our earlier calculations involving lithium and caesium atoms [17, 22]. The calculations are based on the multireference singles and doubles configuration interaction with Davidson correction (MRCISD+Q)
method with atomic effective core potentials and core-polarization potentials, which enables us to treat only three valence electrons explicitly. The full configuration interaction (FCI) method is used to account for the correlation missing in MRCI calculations. An augmented atomic orbital basis allows to obtain reliable Born-Oppenheimer (BO) adiabatic potentials of several molecular states.

All calculations of the BO adiabatic potential energy curves (PECs) and surfaces are performed by means of the MOLPRO program package [23, 24].

The core electrons of the caesium atom are represented by the ECP54SDF pseudopotential [25] and core-polarization potential with the values of dipole polarizability and cut-off parameter taken as $\alpha_D = 15.1\ a_0^3$ and $\rho = 0.17\ a_0^{-2}$,
respectively. In the case of s and p functions, we use the basis set for caesium which comes with the ECP54SDF pseudopotential. For the d and f functions, we use the def2-QZVPPD basis set [26]. Additionally, these basis sets are augmented by the six s functions with the given exponential coefficients of the Gaussian Type Orbitals (GTO) (2.055983, 1.188777, 0.687355, 0.009778, 0.005059,
0.002617), the four p functions (0.695867, 0.293629, 0.004186, 0.001830) and the two d functions (11.281944, 0.003919). In turn, for Li, the core electrons are represented by the ECP2SDF pseudopotential [27] with its respective core-polarization potential parameters ($\alpha_D = 0.1915\ a_0^3$ and $\rho = 0.831\ a_0^{-2}$). Basis set constructed for this pseudopotential is augmented by the six s functions
(392.169555, 77.676373, 15.385230, 0.010159, 0.003894, 0.001493) and the four

3

p functions (19.845562, 4.076012, 0.007058, 0.002598). Additionally, for d and f functions we use the cc-pV5Z basis set [28] augmented by the two d functions (1.043103, 0.026579). We check the quality of our basis sets by performing the CI calculations for the ground states of lithium and caesium atoms as well as for the several excited states of both atoms. The potential energy surfaces for the interaction between the LiCs dimer and the Li atom were computed using the multiconfigurational self-consistent field/complete active space self-consistent field (MCSCF/CASSCF) method to generate the orbitals for the subsequent configuration interaction calculations. The corresponding active space involves the molecular orbitals build from the 6s and 6p valence orbitals of caesium as well as 2s and 2p valence orbitals of lithium. Altogether the active space consists of 5 states in A′ and 2 states in A″ irreducible representations.

In order to determine the quality of our choice, we run dimer calculations for the aforementioned basis sets and pseudpotentials. Our calculated values of the LiCs dimers ground state dissociation energy (D_e = 6090.259 cm^{-1}) and bond length (R_e = 3.6160 Å) are in good agreement with experimental [29] values (D_e = 5875.455 cm^{-1} and R_e = 3.6681 Å).

In order to test the active space and amount of correlation energy that is missing in MRCISD+Q computations, we run FCI calculations, both for the atomization energy of the Li_2Cs trimer and for minima. No difference between the MRCI and FCI results in the atomic limit was found, while the non-zero FCI corrections to atomization and dissociation energies are respectively specified in Tables 1 and 2.

Following Soldan *et al.* [30], we decompose the three-atom interaction potential at the minimum of the ground state into a sum of additive (V_{dimer}) and nonadditive (V_3) contributions. Such decomposition can be expressed as

$$V_{trimer}(r_{12}, r_{13}, r_{23}) = \sum_{i<j} V_{dimer}(r_{ij}) + V_3(r_{12}, r_{13}, r_{23}). \tag{1}$$

To describe the potential energy surfaces of Li + LiCs system we introduce two geometries written in the Z-matrix coordinates. The first geometry starts

4

from the linear LiCs-Li system, where potential energy surfaces are calculated as
a function of two variables. The first of these variables is the distance R between
the Li atom and the Cs atom of the LiCs dimer, while the second variable is
the bond angle θ as is shown in Fig 1. Here, the Li atom approaches the Cs
atom of the dimer. The second geometry, as shown in the geometric scheme in
Fig. 2, is analogical and starts from the linear Li-LiCs system ($\theta = 180^o$), where
the Li atom approaches the dimer from the side on which the other Li atom is
situated. In both geometries, the bond length $R_e = 3.6681$ Å was chosen as it
is the experimental equilibrium distance of the LiCs dimer in the ground state
[29]. Calculations of the BO potential energy surfaces are performed for R in
the range from 4 a_0 to 100 a_0 and from 3.4 a_0 to 100 a_0 for geometries LiCs-Li
and Li-LiCs, respectively, with the various steps adjusted to the atom-molecule
distance. The bond angles are changed from 5° to 180° with the step equal to
5°.

3. Results and discussion

Using the procedure described in the previous chapter we found the global
minima of the ground and first excited doublet A$'$ states of the Li$_2$Cs trimer.
We also calculated the FCI correction to atomization energies. Our results,
compared with those of Żuchowski and Hutson [11] are shown in Table 1. Within
the accuracy of one significant digit (that is given in [11]), our geometry of the
ground state agrees perfectly with the recent study. The result of Richtsmeier
et al. [16] seems to overestimate the Cs-Li bond length and underestimate
the distance between lithium atoms. For the excited-state geometry, there is
a difference between our and Żuchowski and Hutson [11] results. In the case
of our computations, the structure is more compact. The Cs-Li distance is
significantly smaller (by ~ 0.25 Å), while the Li-Li distance is nearly the same.
The atomization energies were calculated by separation of all atoms to the
distances at which energy did not change. To confirm that the internuclear
distances are large enough, we performed FCI computations, that yielded the

5

same energy as MRCI. The value of the atomization energy (Table 1) for $1^2A'$ state from our calculations is larger than the one from the most recent study [11], but at the same time, it is smaller than the one from the earlier paper [16]. In the case of $2^2A'$ state, our atomization energy is again larger in the comparison with value provided by Żuchowski and Hutson [11], while this energy is not reported by Richtsmeier *et al.* [16]. These results are rather expected since the D_e value for the LiCs dimer was already larger than in [11] and we have also used augmented basis sets. On the other hand, the earliest study [16] employed the diatomics-in-molecules technique with parameters derived from experiments on the homonuclear diatomic molecules, since at that time no adequate experimental data were available for heteronuclear diatomics. The FCI corrections are small (less than 0.3%) and suggest, that the choice of active space is reasonable and the MRCI calculations retrieve correlation effects very well. The difference between the ground and first excited doublet A' states energies in the geometric minima, in our and previous results are very close – the difference in [11] is 891 cm^{-1} and in our calculations, it is 889 cm^{-1} with FCI correction and 894 cm^{-1} without. Interestingly, it appears that when the Li$_2$Cs trimer is excited from the ground to the first excited state, the equilibrium geometry bond length between the Li and Cs atoms elongates and the one between Li and Li shortens.

In order to assess the contribution of the nonadditive part of the triatomic interaction energy in the global minimum of the ground state of the Li$_2$Cs molecule, we calculated the interaction energies of the LiCs and Li$_2$ dimers. The interatomic distances used in these calculations R(Cs-Li) and R(Li-Li) (see Table 1) yielded energies 6037 and 7779 cm^{-1} for LiCs and Li$_2$, respectively. Using equation (1), where $r_{12} = r_{13}$ is the R(Cs-Li) and r_{23} is R(Li-Li), we obtained the value of nonadditive contribution V$_3$ which equals -8462 cm^{-1}. It turns out, that since this energy significantly contributes to the atomization energy of the trimer, the simple additive model, that neglects V$_3$, is not suitable for the description of the ground doublet state of the considered trimer.

Calculated BO adiabatic potentials for different states of the Li atom inter-

Table 1: Atomization energies and equilibrium parameters of the ground and first excited doublet states of the Li_2Cs trimer. Results for the 1^2B_2 ($1^2A'$) are compared with results from [16] and [11], whereas 1^2A_1 ($2^2A'$) is compared with results from the supplementary materials therein [31]. Bond lengths are in Å and energies are in cm^{-1} units. This part of calculations were performed with all bond lengths released, but since the equilibrium geometries for both states turned out to be isosceles triangles, only two interatomic distances are given.

	Ground state 1^2B_2 ($1^2A'$)			Excited state 1^2A_1 ($2^2A'$)	
	present	[11]	[16]	present	[31]
Bond lengths					
R (Cs-Li)	3.75	3.8	3.97	4.05	4.3
R (Li-Li)	3.07	3.1	2.67	2.72	2.7*
Energies					
Atomization energies	11390	11073	11507	10496	10182
FCI correction	25	—	—	30	—

* We derived this value from given data using the law of sines.

acting with the LiCs molecule are presented in Figs 1-3. Particularly, comparing Fig. 1 to Fig. 2 one may find a difference in the BO adiabatic potentials for the two considered geometries. As one might expect, when the lithium atom approaches the dimer from the side of the lithium atom (Fig. 2), starting from the bond angle $\theta = 45^o$, there is much more pronounced shape of the potential with a characteristic saddle point around R = 7 a_0 than in the case shown in Fig. 1. In Fig. 2, for $\theta = 30^o$, we observe the appearance of the two minima, one approximately at R equal to 5 a_0 and another close to R = 12 a_0. Generally, it is quite obvious that with decrease of the bond angle θ the potentials' minima shift towards the higher values of R. The reason is that at the short distances the repulsive interaction between the approaching lithium atom and the nearest of dimer's atom grows when θ becomes smaller.

The BO adiabatic potential energy surfaces of the considered geometries of the Li+LiCs system are shown in Fig 3, as well as in the figures with the

7

Table 2: The geometry parameters of Li + LiCs system's minima for the ground and first excited $^2\mathrm{A}'$ states and appropriate dissociation energies D_e. Fixed bond length R_e of the LiCs molecule is equal to 3.6681 Å. Bond lengths are in Å and energies are in cm^{-1} units. The superscript i in $Li^{(i)}$ enumerates lithium atoms.

	Ground state	Excited state
	$1^2\mathrm{A}'$	$2^2\mathrm{A}'$
Bond lengths		
R_e (Cs-Li$^{(2)}$)	3.6681	3.6681
R (Cs-Li$^{(1)}$)	3.79	3.83
R (Li$^{(2)}$-Li$^{(1)}$)	3.06	2.66
Energies		
Dissociation energies	5300	11066
FCI correction	25	35

contour plots placed in the supplementary materials [32]. Analysis of these two surfaces allows us to find minima of the ground state $1^2\mathrm{A}'$ and the first excited state $2^2\mathrm{A}'$ of the lithium atom interacting with the LiCs dimer. The Cs-Li bond length becomes longer after shifting from the minimum of the ground state to the minimum of the excited state, and the Li-Li bond becomes shorter as seen in Table 2. This is analogous to trimer behavior as shown in Table 1. Additionally, the dissociation energies D_e (Table 2), calculated with respect to the Li(2s ^{2}S)+LiCs($1^1\Sigma^+$) and Li(2s ^{2}S)+ LiCs($1^3\Sigma^+$) channels are equal respectively to 5300 and 11066 cm^{-1} for the $1^2\mathrm{A}'$ and $2^2\mathrm{A}'$ states.

As long as we keep the distance R_e between atoms in the LiCs molecule fixed, we are able to investigate the conical intersections (CI) of the potential energy surfaces in both considered approaches (LiCs-Li and Li-LiCs) as single points only. The three of such CI points are found. Figure 4 presents colored contour plots of differences between BO adiabatic PESs of the ground $1^2\mathrm{A}'$ state and the first excited $2^2\mathrm{A}'$ state of the LiCs-Li (upper panel) and Li-LiCs (lower panel) geometries of the system, where conical intersection points are clearly

8

visible. The most important conical intersection is the point lying on the seam

in the C_{2v} symmetry. This symmetry introduces the interplay between 1^2B_2 and 1^2A_1 electronic states corresponding to $1^2A'$ and $2^2A'$ in the C_s symmetry, i.e. the two lowest lying potential energy surfaces. In our case, we find this conical intersection by setting the distance between the LiCs molecule and the approaching lithium atom to the value equal R_e and finding the angle, for which such calculated potential energy curves cross. The CI determined in that way is visible in both geometries (both panels), as shown in Fig 4. In this point the Li + LiCs system is the isosceles triangle with angles equal to 38.10 (Li-Cs-Li, upper panel) and 70.95 (Li-Li-Cs, lower panel) degrees, as well as bond lengths amount to 6.9317 (LiCs-Li) and 4.5241 (Li-LiCs) a_0. The energy of this CI equals 3264 cm^{-1} below the Li(2s ^{2}S) + LiCs($1^1\Sigma^+$) dissociation limit. The two other conical intersections are situated in the repulsive parts of the PESs. The first one is visible in the upper panel of Fig 4 where the angle Li-Cs-Li equals 24.13 degrees and the distance LiCs-Li is 5.0640 a_0. It is not visible in the lower panel since in the Li-LiCs geometry coordinates, equal to 41.86 degrees and 3.1021 a_0, fall out of the shown range. The second one (see the lower panel) is present at the angle Li-Li-Cs equals 20.35 degrees and distance Li-LiCs equals 8.5253 a_0. This one is not visible in the upper panel, since its coordinates for the LiCs-Li geometry, equal to 109.70 degrees and 3.1490 a_0, are out of the presented range. The respective energies of these conical intersections are 14331 and 18713 cm^{-1} above the Li(2s ^{2}S) + LiCs($1^1\Sigma^+$) dissociation limit.

Fig 5 presents the BO adiabatic potentials of the first two doublet Σ^+ states (a), first quartet Σ^+ states (b), first doublet Π states (c) and first quartet Π states (d) of the linear Li + LiCs system for the two considered geometrical cases with the interatomic distance R_e in the LiCs molecule fixed. These potential energy curves correlate with the three lowest-lying dissociation limits. The $1^2\Sigma^+$ states correlate to the asymptote where both the lithium atom and the LiCs molecule are in the ground states, namely Li(2s ^{2}S) and LiCs($1^1\Sigma^+$), respectively. The dissociation limit for the $2^2\Sigma^+$ and $1^4\Sigma^+$ states corresponds to the sum of the first excited triplet state ($1^3\Sigma^+$) energy of the LiCs molecule

9

215 and the ground state energy of the lithium atom. Finally, the $1^2\Pi$ and $1^4\Pi$ states correlate with the dissociation limit, where the Li atom is in the 2s ^{2}S state, whereas the LiCs molecule is in the $1^3\Pi$ state.

All potentials presented in Fig 5 show smooth behavior. It is clearly visible that the differences in the positions of the minima and their depths depend 220 on the atoms arrangement. In the case of LiCs-Li arrangement, the repulsive interaction between the approaching Li atom and the Cs atom of the diatomic molecule is much stronger than in the case of Li-LiCs, where we deal with the repulsion between two lithium atoms. Generally, in the case of LiCs-Li geometry, it leads to more shallow potentials and move their equilibrium positions to larger 225 distances between LiCs molecule and Li atom. The opposite situation exits for Li-LiCs geometry, where potential energy curves are deeper and their minima lying middlingly 2.4 a_0 closer in the comparison with previous case. It is also worth to notice, that in the considered Li + LiCs system the doublet states are usually deeper than the quartet states.

230 All of our calculated potential energy surfaces, potential energy curves in the case of linear arrangement of the Li + LiCs system and contour plots of presented in the manuscript surfaces are available in the supplementary materials for this article [32] and on the group's website [33].

4. Conclusions

235 The results of the *ab initio* electronic structure calculations for the Li_2Cs trimer, as well as the potential energy surfaces of the Li + LiCs system have been presented. The global minima of the ground and first excited doublet A′ states were found and compared with other theoretical results. The three-body nonadditive interactions were calculated for the global minimum of the ground 240 doublet A′ state, and it turned out, that the simple additive model of dimer interactions is not suitable for the description of this state. The agreement between the present and previous studies is good, although there are some differences in the geometry of the excited state.

10

Analysis of the potential energy surfaces has shown characteristic features of the BO adiabatic potentials describing the approach of the lithium atom to the LiCs dimer in its ground and low-lying excited electronic states. We have found substantial differences between potential energy surfaces calculated for different approach directions of the lithium atom. The three conical intersection points have also been found on these surfaces and thoroughly discussed.

Results of our calculations provide insight into the structure of Li_2Cs trimer and interaction between the lithium atom with the LiCs diatomic molecule. It could be useful for researchers dealing with spectroscopic measurements of the three-body alkali systems, experiments involving collisions of alkali atoms with heteronuclear alkali diatomic molecules as well as on the cold and ultracold polar alkali molecules.

[1] J. Nagl, G. Auböck, A. W. Hauser, O. Allard, C. Callegari, W. E. Ernst, Heteronuclear and homonuclear high-spin alkali trimers on helium nanodroplets, Phys. Rev. Lett. 100 (2008) 063001. `doi:10.1103/PhysRevLett.100.063001`.
URL `https://link.aps.org/doi/10.1103/PhysRevLett.100.063001`

[2] J. Nagl, G. Auböck, A. W. Hauser, O. Allard, C. Callegari, W. E. Ernst, High-spin alkali trimers on helium nanodroplets: Spectral separation and analysis, The Journal of Chemical Physics 128 (2008) 154320. `doi:10.1063/1.2906120`.
URL `https://doi.org/10.1063/1.2906120`

11

[3] A. W. Hauser, C. Callegari, P. Soldán, W. E. Ernst, On the doublet states of the potassium trimer, The Journal of Chemical Physics 129 (2008) 044307.

275   doi:10.1063/1.2956492.

URL https://doi.org/10.1063/1.2956492

[4] A. W. Hauser, W. E. Ernst, Homo- and heteronuclear alkali metal trimers formed on helium nanodroplets. Part I. Vibronic spectra simulations based on ab initio calculations, Phys. Chem. Chem. Phys. 13 (2011) 18762–18768.

280   doi:10.1039/C1CP21163C.

URL http://dx.doi.org/10.1039/C1CP21163C

[5] C. Giese, F. Stienkemeier, M. Mudrich, A. W. Hauser, W. E. Ernst, Homo- and heteronuclear alkali metal trimers formed on helium nanodroplets. Part II. Femtosecond spectroscopy and spectra assignments, Phys. Chem. Chem.

285   Phys. 13 (2011) 18769–18780. doi:10.1039/C1CP21191A.

URL http://dx.doi.org/10.1039/C1CP21191A

[6] S. Vajda, S. Rutz, J. Heufelder, P. Rosendo, H. Ruppe, P. Wetzel, L. Wöste, Observation of predissociated excited states in mixed alkali trimer clusters Na_2K and K_2Na: time-resolved spectroscopy of boundfree transitions, The

290   Journal of Physical Chemistry A 102 (1998) 4066–4068. doi:10.1021/jp9802984.

URL 10.1021/jp9802984

[7] A. Lindinger, C. Lupulescu, A. Bartelt, S. Vajda, L. Wöste, Coherent control of alkali cluster fragmentation dynamics, Spectrochim-

295   ica Acta Part B: Atomic Spectroscopy 58 (2003) 1109 – 1124. doi:10.1016/S0584-8547(03)00067-3.

URL   http://www.sciencedirect.com/science/article/pii/S0584854703000673

[8] S. A. Moses, J. P. Covey, M. T. Miecnikowski, B. Yan, B. Gadway, J. Ye,

300   D. S. Jin, Creation of a low-entropy quantum gas of polar molecules in an optical lattice, Science 350 (2015) 659–662. doi:10.1126/science.

12

aac6400.

URL http://science.sciencemag.org/content/350/6261/659

[9] J. Ulmanis, J. Deiglmayr, M. Repp, R. Wester, M. Weidemuüller, Ultra-
cold molecules formed by photoassociation: Heteronuclear dimers, inelastic
collisions, and interactions with ultrashort laser pulses, Chemical Reviews
112 (2012) 4890–4927. doi:10.1021/cr300215h.

[10] P. Soldán, Lowest quartet states of heteronuclear alkali-metal trimers, Phys.
Rev. A 82 (2010) 034701. doi:10.1103/PhysRevA.82.034701.
URL http://link.aps.org/doi/10.1103/PhysRevA.82.034701

[11] P. S. Żuchowski, J. M. Hutson, Reactions of ultracold alkali-metal dimers,
Phys. Rev. A 81 (2010) 060703. doi:10.1103/PhysRevA.81.060703.
URL http://link.aps.org/doi/10.1103/PhysRevA.81.060703

[12] H. Jing, J. Cheng, P. Meystre, Coherent generation of triatomic molecules
from ultracold atoms, Phys. Rev. A 77 (2008) 043614. doi:10.1103/
PhysRevA.77.043614.
URL http://link.aps.org/doi/10.1103/PhysRevA.77.043614

[13] K. Kato, Y. Wang, J. Kobayashi, P. S. Julienne, S. Inouye, Isotopic Shift
of Atom-Dimer Efimov Resonances in K-Rb Mixtures: Critical Effect of
Multichannel Feshbach Physics, Phys. Rev. Lett. 118 (2017) 163401. doi:
10.1103/PhysRevLett.118.163401.
URL https://link.aps.org/doi/10.1103/PhysRevLett.118.163401

[14] A. Harter, A. Krukow, M. Deisz, B. Drews, E. Tiemann, J. H. Denschlag,
Population distribution of product states following three-body recombina-
tion in an ultracold atomic gas, Nat Phys 9 (8) (2013) 512–517.
URL http://dx.doi.org/10.1038/nphys2661

[15] S. A. Moses, J. P. Covey, M. T. Miecnikowski, D. S. Jin, J. Ye, New frontiers
for quantum gases of polar molecules, Nat Phys 13 (2017) 13–20. doi:

13

10.1038/nphys3985;.

330   URL http://dx.doi.org/10.1038/nphys3985

[16] S. C. Richtsmeier, M. L. Hendewerk, D. A. Dixon, J. L. Gole, Structure
     of mixed alkali metal trimers, The Journal of Physical Chemistry 86 (20)
     (1982) 3932–3937. doi:10.1021/j100217a010.

[17] P. Jasik, J. Sienkiewicz, Calculation of adiabatic potentials of Li_2, Chemical
335   Physics 323 (2006) 563 – 573. doi:10.1016/j.chemphys.2005.10.025.
     URL   http://www.sciencedirect.com/science/article/pii/
     S0301010405005380

[18] P. Jasik, J. Wilczyński, J. E. Sienkiewicz, Calculation of adiabatic poten-
     tials of Li_2^+, The European Physical Journal Special Topics 144 (1) (2007)
340   85–91. doi:10.1140/epjst/e2007-00111-2.
     URL https://doi.org/10.1140/epjst/e2007-00111-2

[19] Ł. Miądowicz, P. Jasik, J. E. Sienkiewicz, Possible schemes of photoassoci-
     ation processes in the KLi molecule with newly calculated potential energy
     curves, Central European Journal of Physics 11 (9) (2013) 1115–1122.
345   doi:10.2478/s11534-013-0199-z.
     URL   https://www.degruyter.com/view/j/phys.2013.11.issue-9/
     s11534-013-0199-z/s11534-013-0199-z.xml

[20] P. Łobacz, P. Jasik, J. E. Sienkiewicz, Theoretical study of highly-excited
     states of KRb molecule, Central European Journal of Physics 11 (9) (2013)
350   1107–1114. doi:10.2478/s11534-012-0137-5.
     URL http://dx.doi.org/10.2478/s11534-012-0137-5

[21] M. Wiatr, P. Jasik, J. E. Sienkiewicz, The adiabatic potentials of low-
     lying electronic states of the NaRb molecule, Physica Scripta 90 (5) (2015)
     054012.
355   URL http://stacks.iop.org/1402-4896/90/i=5/a=054012

14

[22] J. Szczepkowski, P. Jasik, A. Grochola, W. Jastrzębski, J. E. Sienkiewicz, P. Kowalczyk, The $4^1\Sigma^+$ electronic state of LiCs molecule, The European Physical Journal Special Topics 222 (9) (2013) 2329–2333. `doi:10.1140/epjst/e2013-02013-0`.

360   URL `http://dx.doi.org/10.1140/epjst/e2013-02013-0`

[23] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, Molpro: a general purpose quantum chemistry program package, WIREs Comput Mol Sci 2 (2012) 242–253.

[24] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, 365 W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, 370 M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, Molpro, version 2012.1, a package of ab initio programs, see `http://www.molpro.net` (2015).

[25] L. V. Szentpaly, P. Fuentealba, H. Preuss, H. Stoll, Pseudopoten-375 tial calculations on Rb_2^+, Cs_2^+, RbH^+, CsH^+ and the mixed alkali dimer ions, Chemical Physics Letters 93 (6) (1982) 555 – 559. `doi:http://dx.doi.org/10.1016/0009-2614(82)83728-7`.
URL   `http://www.sciencedirect.com/science/article/pii/0009261482837287`

380 [26] D. Rappoport, F. Furche, Property-optimized gaussian basis sets for molecular response calculations, The Journal of Chemical Physics 133 (13) (2010) 134105. `doi:http://dx.doi.org/10.1063/1.3484283`.
URL   `http://scitation.aip.org/content/aip/journal/jcp/133/13/10.1063/1.3484283`

15

[27] P. Fuentealba, H. Preuss, H. Stoll, L. V. Szentpaly, A proper account of core-polarization with pseudopotentials: single valence-electron alkali compounds, Chemical Physics Letters 89 (5) (1982) 418 – 422. doi:http://dx.doi.org/10.1016/0009-2614(82)80012-2.
URL http://www.sciencedirect.com/science/article/pii/0009261482800122

[28] B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, A. K. Wilson, Gaussian basis sets for use in correlated molecular calculations. VII. Valence, core-valence, and scalar relativistic basis sets for Li, Be, Na, and Mg, Theoretical Chemistry Accounts 128 (1) (2011) 69–82. doi:10.1007/s00214-010-0764-0.
URL http://dx.doi.org/10.1007/s00214-010-0764-0

[29] P. Staanum, A. Pashov, H. Knöckel, E. Tiemann, $X^1\Sigma^+$ and $a^3\Sigma^+$ states of LiCs studied by Fourier-transform spectroscopy, Phys. Rev. A 75 (2007) 042513. doi:10.1103/PhysRevA.75.042513.
URL http://link.aps.org/doi/10.1103/PhysRevA.75.042513

[30] P. Soldán, M. T. Cvitaš, J. M. Hutson, Three-body nonadditive forces between spin-polarized alkali-metal atoms, Phys. Rev. A 67 (2003) 054702. doi:10.1103/PhysRevA.67.054702.
URL https://link.aps.org/doi/10.1103/PhysRevA.67.054702

[31] P. S. Żuchowski, J. M. Hutson, Supplementary materials for, Phys. Rev. A 81 (2010) 060703. doi:10.1103/PhysRevA.81.060703.
URL https://journals.aps.org/pra/supplemental/10.1103/PhysRevA.81.060703

[32] See electronic supplementary materials document no. *(number will be inserted by Editor)*.

[33] Potential energy surfaces of the Li + LiCs system in the tabular form.
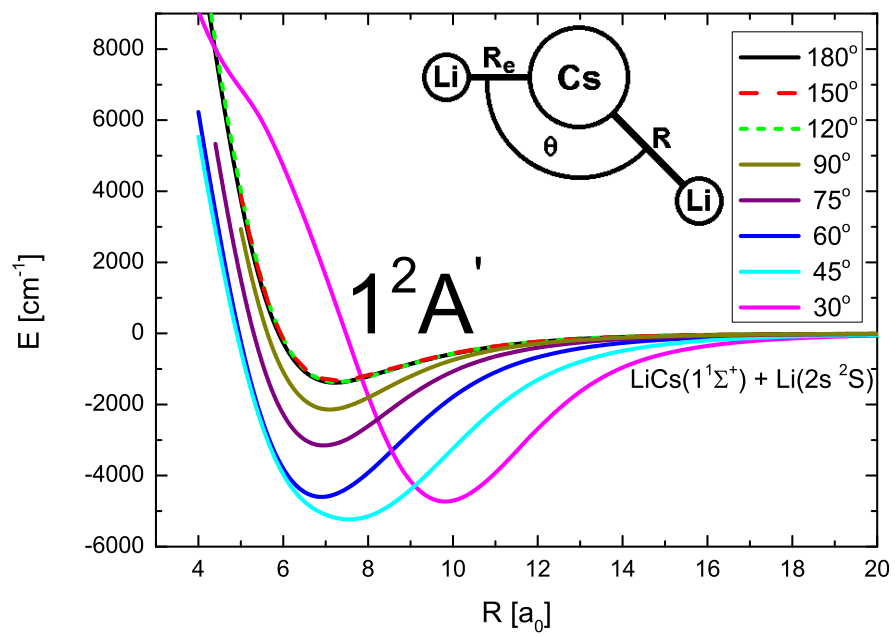URL http://aqualung.mif.pg.gda.pl/results/li+lics/

16

Figure 1: BO adiabatic potential energy curves of the ground state of the system in the LiCs-Li geometry, calculated for eight different angles.
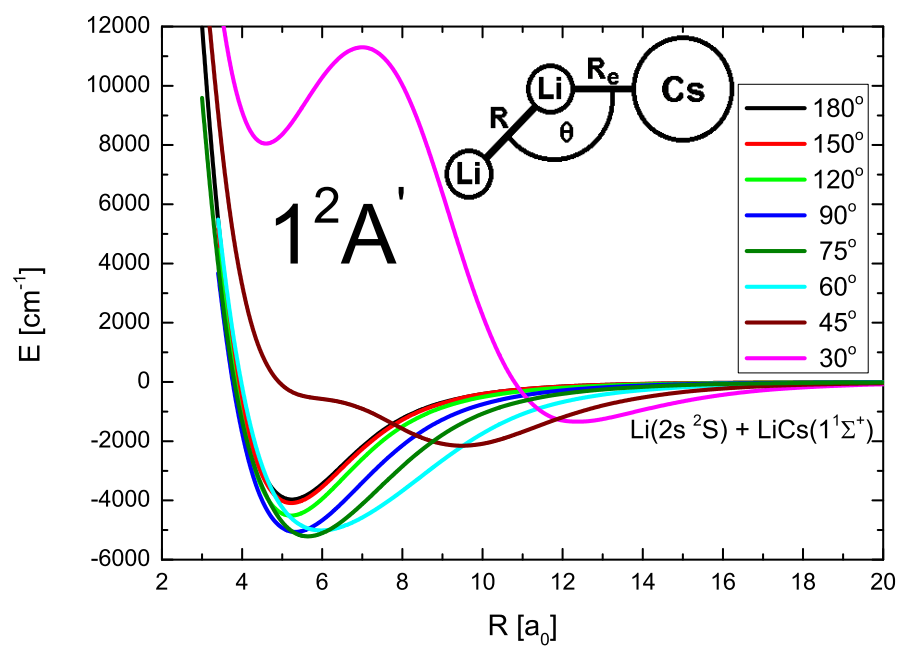
Figure 2: BO adiabatic potential energy curves of the ground state of the system in the Li-LiCs geometry, calculated for eight different angles.
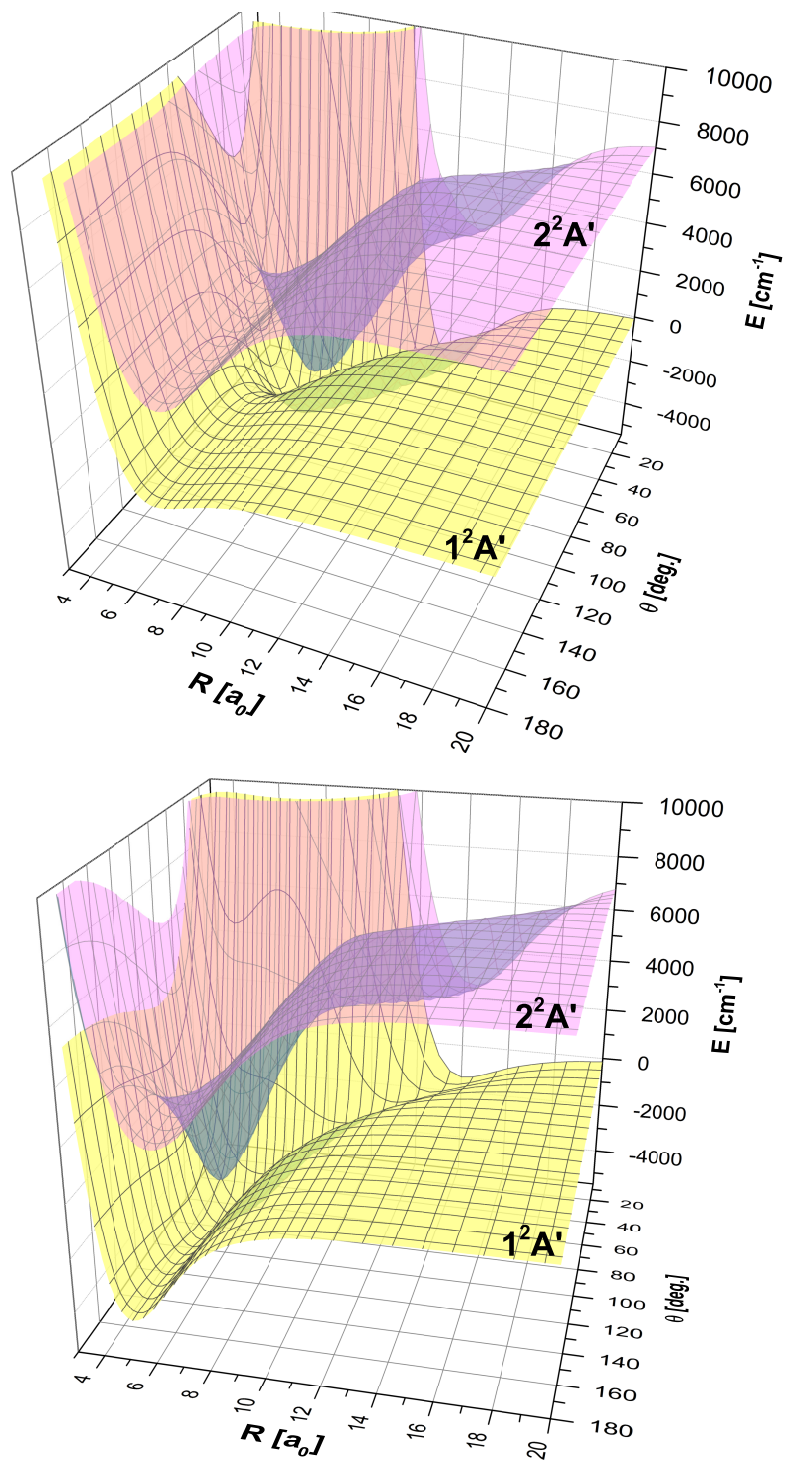
18

Figure 3: BO adiabatic potential energy surfaces of the ground $1^2A'$ state and first excited $2^2A'$ state of the LiCs-Li (upper panel) and Li-LiCs (lower panel) geometries of the system.
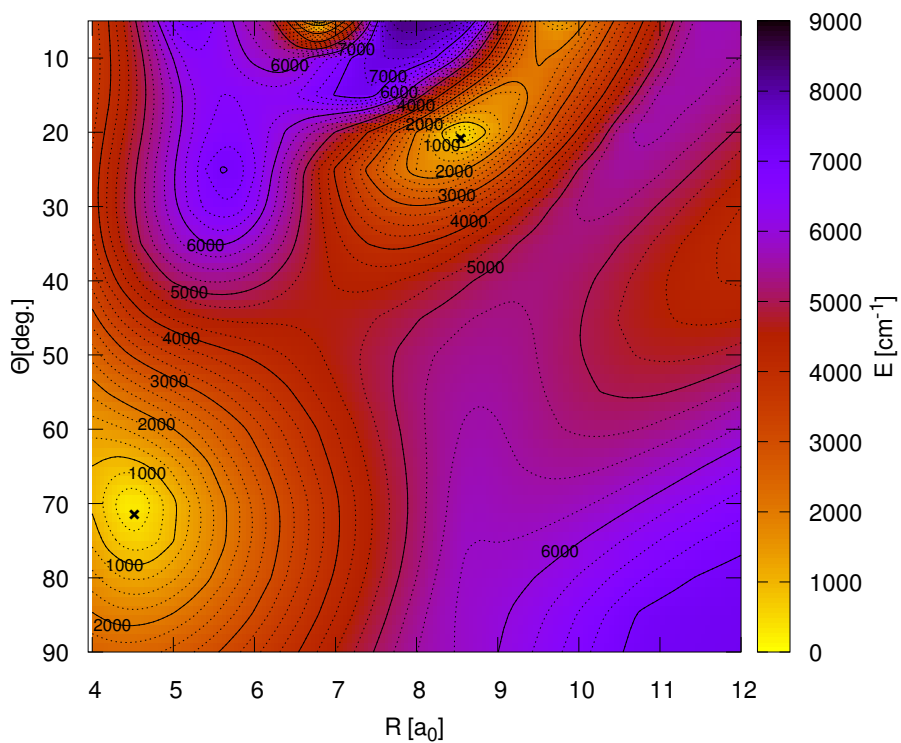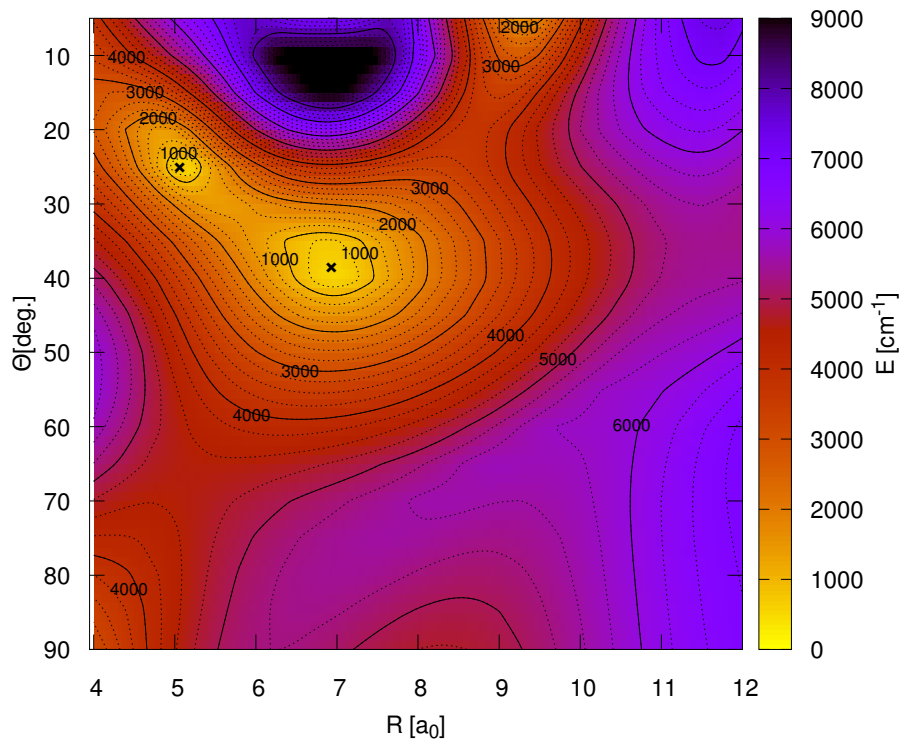
Figure 4: Contour plots of differences (in cm^{-1}) between BO adiabatic potential energy surfaces of the ground $1^2A'$ state and first excited $2^2A'$ state of the LiCs-Li (upper panel) and Li-LiCs (lower panel) geometries of the system. The conical intersection points are marked by **x**.
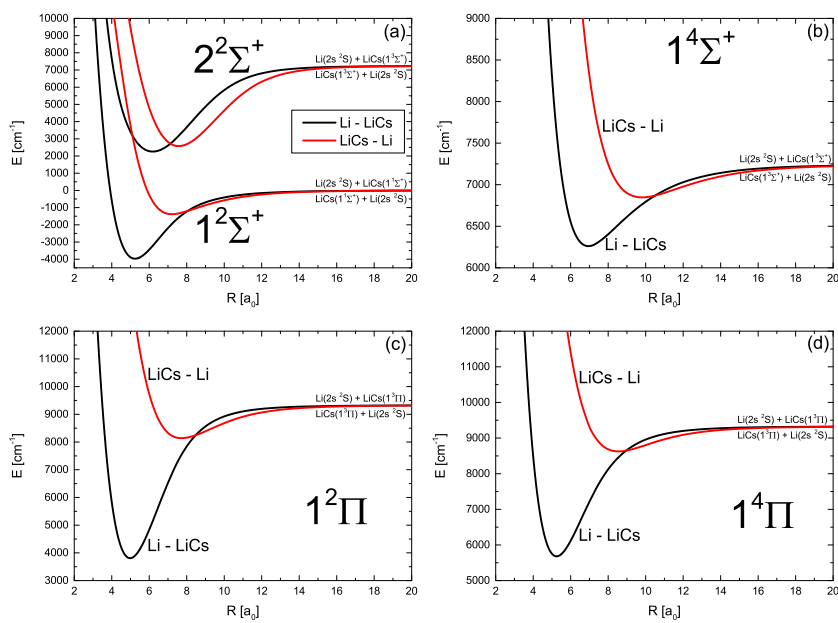
Figure 5: BO adiabatic potential energy curves of the $1,2^2\Sigma^+$ (a), $1^4\Sigma^+$ (b), $1^2\Pi$ (c) and $1^4\Pi$ (d) states of the two linear geometries. The red and black lines refer to LiCs-Li and Li-LiCs geometries, respectively.