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Ab initio study of the ground and several excited states of the NLi system

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Abstract

Using mainly CASSCF/cc-pVTZ ab initio methods we have computed the ground $X^3\Sigma^-$ and several excited states of the NLi species. In particular, we calculated full potential energy curves of the $X^3\Sigma^-$, $^5\Sigma^-$ (dissociative), $A^3\Pi$, $a^1\Delta$, $b^1\Sigma^+$, $B^3\Sigma^-$, $c^1\Pi$, $C^3\Pi$ and $d^1\Pi$ states. For six of these states the molecular constants ω_e, $\omega_e\chi_e$, α_e and $\overline{D}_e$ have also been obtained. For the ground $X^3\Sigma^-$ state a dissociation energy $D_e = 29.5$ kcal mol^{-1} has been calculated at the MR-CISD level.

1. Introduction

Nitrenes are molecules of the general type N–R, with the simplest nitrene being N–H. Lithium nitrene, N–Li, is formally similar to NH, but although the latter has been studied exhaustively both experimentally and theoretically, the former has attracted little attention. An early experimental dissociation energy estimate [1] of NLi gives $D = 111-178$ kcal mol^{-1}, while a more recent experimental estimate by Herm and Herschbach [2] locates this dissociation energy at about 50 kcal mol^{-1}. These suggestions were based on an ionic model of NLi, while the diverging numerical values given are due to the different parameters employed by each group [1,2], that is, different affinities of the N atom and N–Li bond distances. By now we know that the lower D value is much more realistic, but overestimated by perhaps 10–15 kcal mol^{-1} (vide infra).

The first ab initio work on NLi at the CISD level with the six $1\sigma^2 2\sigma^2 3\sigma^2$ inner electrons kept frozen and a DZ + P Slater basis, by Dykstra et al. [3], appeared twenty years ago. These workers focused on the $X^3\Sigma^-$ and $A^3\Pi$ states of the NLi molecule. By Khait and Baranovskii [4], seven low-lying states for the NLi species were calculated at the SCF-DZ level. It is worth noting at this point, that at the SCF level the $X^3\Sigma^-$ state of NLi is unbound (vide infra). Recently Boldyrev et al. [5], reported ab initio results of lithium containing molecules and molecular ions. For the NLi species these researchers have calculated at the MP2/6-311 + G* level the equilibrium geometries of the $X^3\Sigma^-$, $^3\Pi_i$, $^3\Pi_r$ and $^1\Sigma^+$ states. For the ground $X^3\Sigma^-$ state only and at the MP4, QCISD(T)/6-311 + G(2df)//MP2 level, the dissociation energy was also computed [5].

With the purpose of obtaining more uniform and extended results on the NLi molecule we report here CASSCF + 1 + 2 (multi reference complete active space + single + double replacements; MR-CISD)

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full potential energy curves for the $X^3\Sigma^-$, $^5\Sigma^-$ (dissociative), $A^3\Pi$, $a^1\Delta$, $b^1\Sigma^+$, $B^3\Sigma^-$, $c^1\Pi$, $C^3\Pi$ and $d^1\Pi$ states. In addition, we are trying to interpret our findings using simple valence bond–Lewis diagrams, which in most cases offer an intuitive understanding of chemical binding.

2. Computational approach

The Dunning [6] augmented-cc-pVTZ basis set 11s6p3d2f contracted to 5s4p3d2f was employed for the N atom. For the Li atom a 9s4p contracted to 4s2p basis was used; the s functions were taken from the Duijneveldt [7] compilation while the p functions are those of Dunning and Hay [7]. Over all the [5s4p3d2f/4s2p] basis is comprised of 56 contracted Gaussians.

The computational methods used are SCF, CASSCF, CASSCF + 1 + 2 (MR-CISD) and CISD. All calculations were done under C_{2v} symmetry restrictions with the $1\sigma^2 2\sigma^2 \sim 1s_N^2 1s_{Li}^2$ core electrons kept frozen (inactive), while the active space was always consisted of six orbitals of the appropriate symmetry hosting the six valence electrons. The number of the configuration state functions (CSFs) arising from this six-to-six CAS, range from 33 ($c^1\Pi$) to 75 ($b^1\Sigma^+$). The CI space on top of the CAS ranges from approximately 35000 ($a^1\Delta$) to 58000 ($X^3\Sigma^-$) CSFs. Unfreezing the $2\sigma^2$ ($\sim 1s_{Li}^2$) electrons in the $X^3\Sigma^-$ state had a rather small effect on the calculated properties at the CISD level, so we did not pursue this approach any further.

From the MR-CISD potential energy curves, by fitting the calculated points up to a distance of 2.5–3.0 Å to a seven degree polynomial and applying perturbation techniques [8], the spectroscopic constants ω_e, $\omega_e\chi_e$, α_e and $\overline{D}_e$ were extracted.

All our calculations were done on the Alpha AXP 300X workstation of the Physical Chemistry Laboratory using the COLUMBUS [9] and MELD [10] codes.

3. Results and discussion

We will discuss each investigated state separately. Table 1 summarizes all our pertinent results; for reasons of comparison and completeness the ab initio results of previous researchers [3,5] are also presented. Fig. 1 shows all the MR-CISD potential energy curves studied in this Letter.

3.1. Ground, $X^3\Sigma^-$ state

The molecule traces its lineage to the N and Li atoms in their ground states. The bond formation can be represented adequately by the valence bond–Lewis diagrams, see Scheme 1.

From Table 1 we observe that the molecule is unbound at the SCF level, becomes bound at the CASSCF level while it more than doubles its binding energy at the MR-CISD (dynamical correlation) level. At the 'MR-CISD + DV' (extrapolation to the full-CI using the (modified) Davidson formula [11]) level, the dissociation energy increases by 2 kcal mol^{-1}, so the final $D_e = 31.7$ kcal mol^{-1} is in practical agreement with the results of Ref. [5]. Keep in mind though that comparisons with the results of Ref. [5] are not straightforward due to the entirely different methodology and/or strategy used by these workers. The very low D_e value obtained by Dykstra et al. [3], 19.6 kcal mol^{-1}, is mainly due to the insufficient amount of correlation energy recovered in this work. We also remind that in Ref. [3], six electrons were kept frozen in the correlated calculation, thus total energies cannot be directly compared. Concerning the results of Ref. [5] and given the aforementioned reservations, we predict a much longer bond distance, the difference being ≈ 0.05 Å at the MR-CISD (or MR-CISD + DV) level. As expected the molecule is very ionic with a dipole moment of 7.15 D at the CISD level.

3.2. First excited, $A^3\Pi$ state

The asymptotic atomic states of this symmetry are the ground state of the N atom and the first excited state of the Li atom. For the used icons see Scheme 2. In more traditional terms we can claim that the two atoms are held together by a π-bond (π_x^2), another half π-bond ($1\pi_y^1$) and a half σ-bond ($4\sigma^1$), and of course, a shorter bond length and a larger intrinsic bond strength are expected as compared to the $X^3\Sigma^-$ state. This is exactly what happens: from Table 1 we observe that at the MR-CISD level the

bond length shortens by 0.15 Å and the internal bond strength increases by 35 kcal mol^{-1}. Essentially identical differences between the $X^3\Sigma^-$ and $A^3\Pi$ states are observed in Refs. [3,5].

Fig. 1 shows the $A^3\Pi$ potential energy curve. The calculated energy gap T_e is 7.5 kcal mol^{-1}, in agreement with Ref. [3], but by 1.6 kcal mol^{-1} larger than that of Ref. [5]. This is a very low-lying state, therefore the $\Delta E(^2P \leftarrow {}^2S)$ splitting of the Li atom should be calculated accurately enough. Our calculated $\Delta E(^2P \leftarrow {}^2S;\ Li)$ is 1.85 eV with the experimental [12] value being 1.846 eV. Finally, from the population analysis at the CISD level we conclude that the $A^3\Pi$ state is equally ionic with the

Table 1
Absolute energies E (hartree), dissociation energies D_e (kcal mol^{-1}), equilibrium bond distances R_e (Å), Mulliken charges q_N, dipole moments μ (D), spectroscopic constants ω_e, $\omega_e\chi_e$, α_e, $\overline{D}_e$ (cm^{-1}) for the ground $X^3\Sigma^-$ state and several excited states of the NLi molecular system. T_e (kcal mol^{-1}) is the energy gap ΔE (excited state $\leftarrow X^3\Sigma^-$)

State	Method	$-E$	D_e	R_e	q_N	μ	ω_e	$\omega_e\chi_e$	α_e	$\overline{D}_e \times 10^{-6}$	T_e [g]
$X^3\Sigma^-$	SCF	61.82280	−4.4	1.885	−0.67	7.17					0.0
	CASSCF	61.86370	14.1	1.933							0.0
	MR-CISD	61.98909	29.5	1.921			619.9	7.07	0.0165	9.7	0.0
	MR-CISD + DV	61.9964	31.7	1.930							0.0
	CISD	61.98241	23.7	1.905	−0.61	7.15					0.0
	CISD [j]	61.7781 [a]	19.6 [a]	1.85 [a]		7.0 [b]	657.0 [a]	13.97 [a]	0.0167 [a]	–	0.0
	MP2/QCISD(T) [k]	–	34.4 [c]	1.874 [d]	−0.85		681.0 [d]				0.0
$A^3\Pi$	SCF	61.81039	36.6 [e]	1.736	−0.68						7.78
	CASSCF	61.85343	50.3 [e]	1.764							6.41
	MR-CISD	61.97713	64.6 [e]	1.772			731.2	6.45	0.0170	11.4	7.47
	MR-CISD + DV	61.9841	66.5 [e]	1.776							7.72
	CISD	61.97124	59.2 [e]	1.749	−0.62	5.99					7.01
	CISD [j]	61.8656 [a]	53.0 [e]	1.70 [a]		6.20 [b]	833.0 [a]	7.99 [a]	0.0150 [a]		7.84
	MP2/QCISD(T) [k]	–	–	1.728 [d]			787.0 [d]				5.90
$a^1\Delta$	SCF	61.76478	23.9 [f]	1.863	−0.66						36.4
	CASSCF	61.80433	31.4 [f]	1.873							37.3
	MR-CISD	61.93404	53.7 [f]	1.894			653.3	3.16	0.014	9.47	34.5
	MR-CISD + DV	61.9419	56.4 [f]	1.906							34.2
$b^1\Sigma^+$	CASSCF	61.81697	59.5 [h]	1.892							29.9
	MR-CISD	61.92578	58.3 [h]	1.886		(6.87) [a]	675.35	5.61	0.0144	9.14	39.7
	MR-CISD + DV	61.9397	53.7 [h]	1.884							35.6
	MP2/QCISD(T) [k]	–	–	1.640 [d]			1099.0 [d]				49.0
$B^3\Sigma^-$	CASSCF	61.79907	23.0 [e]	2.089							40.6
	MR-CISD	61.91624	26.8 [e]	2.194		(0.02) [a]	434.93	1.10	0.094	11.2	45.7
	MR-CISD + DV	61.9241	28.8 [e]	2.265							45.4
$c^1\Pi$	CASSCF	61.79243	40.4 [h]	1.775							44.7
	MR-CISD	61.91884	50.0 [h]	1.794			679.54	5.25	0.017	12.2	44.1
$C^3\Pi$	CASSCF	61.86347	15.7 [h]	3.088							79.0
	MP2/QCISD(T) [k]	–		2.308							97.8
$d^1\Pi$	MR-CISD	61.80365	9.0 [i]	3.362							116.0

[a] CISD values. [b] SCF values. [c] QCISD(T) 6-311 + G(2df)||MP2(full)/6-311 + G*. [d] MP2(full)/6-311 + G*.
[e] With respect to N(^{4}S) + Li(^{2}P) ('internal bond strength'). [f] With respect to N(^{2}D) + Li(^{2}S). [g] With respect to $X^3\Sigma^-$.
[h] With respect to N(^{2}P) + Li(^{2}S). [i] With respect to N(^{2}D) + Li(^{2}P). [j] Ref. [3]. [k] Ref. [5].

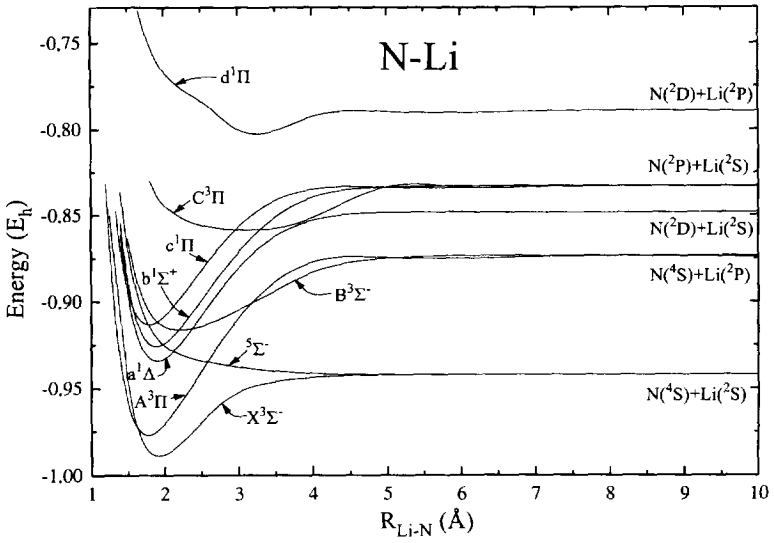


Fig. 1. Potential energy curves for the ground $X^3\Sigma^-$ and several excited states of the NLi molecule at the MR-CISD level of theory. All energies are shifted by 61.0 E_h.

$X^3\Sigma^-$ state, while its smaller dipole moment reflects its shorter bond length.

3.3. $^5\Sigma^-$

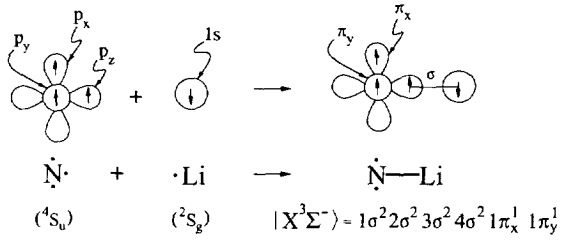
The potential energy curve of this obviously dissociative state, stemming from the ground state atoms, is depicted in Fig. 1.

3.4. $a\,^1\Delta$

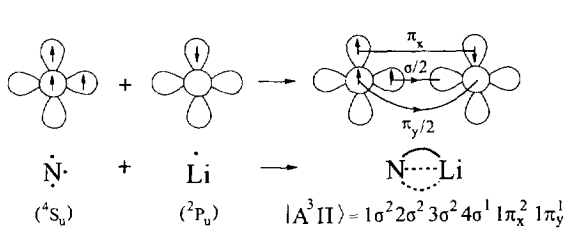
This state traces its lineage to the first excited ^2D_u state of the N atom and the ground state of the Li atom, Fig. 1. It has the same electronic configuration with that of the $X^3\Sigma^-$ state, but the symmetry carrying π^2 electrons are coupled into an open singlet. The experimental [12] energy gap $\Delta E(^2D \leftarrow {}^4S)$ of the N atom is 2.384 eV while at the MR-CISD level the calculated splitting is 2.54 eV, 3.6 kcal mol^{-1} larger. Downshifting uniformly the $a\,^1\Delta$ potential curve our correlated 34.5 kcal mol^{-1} T_e value, Table 1, decreases by the same amount.

3.5. $b\,^1\Sigma^+$

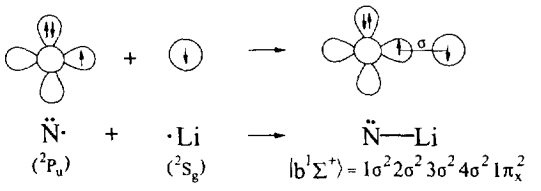
According to Fig. 1 the $b\,^1\Sigma^+$ state dissociates adiabatically to the ^2P_u excited state of the N atom and the ground state of the Li atom. Pictorially, see Scheme 3 with the π^2 electrons coupled into a Σ^+ symmetry. The calculated energy difference $\Delta E(^2P \leftarrow {}^4S; N) = 3.02$ eV is underestimated by 0.58 eV as compared to the experimental [12] one. Upshifting this time uniformly the $b\,^1\Sigma^+$ potential energy curve increases the calculated 39.7 kcal mol^{-1} T_e value by an equal amount, therefore changing the order of this curve with respect to the $B\,^3\Sigma^-$ curve, putting the $b\,^1\Sigma^+$ state approximately 6 kcal mol^{-1} above the



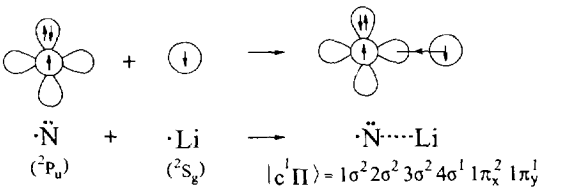
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 5.

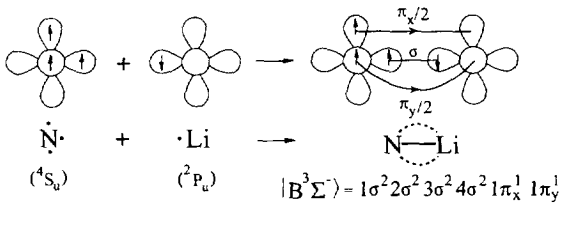
$B\,^3\Sigma^-$ state. At the same time due to the opposite shiftings of the $a\,^1\Delta$ and $b\,^1\Sigma^+$ curves by 3.6 and 13.4 kcal mol^{-1} respectively the energy gap between these two states increases by approximately 17 kcal mol^{-1}, so the final $b\,^1\Sigma^+ \leftarrow a\,^1\Delta$ gap becomes ≈ 22 kcal mol^{-1} instead of 5.2 kcal mol^{-1} reported in Table 1. From Table 1 we observe that our MR-CISD bond distance differs dramatically from the corresponding result by Boldyrev et al. [5], ours being much larger. It is interesting that when corrected by 13.4 kcal mol^{-1} the T_e value at the MR-CISD + DV level agrees exactly with that of Ref. [5], which is 49.0 kcal mol^{-1}.

3.6. $B\,^3\Sigma^-$

The asymptotic products of the $B\,^3\Sigma^-$ state are the ground state of the N atom and the first excited state of the Li atom. Schematically, see Scheme 4. This is bound, with respect to the asymptotic product states, by 27 kcal mol^{-1} with a T_e of 47.5 kcal mol^{-1} at the MR-CISD level, Table 1. Although it is of the same symmetry as the ground state its binding mode is of completely different nature: it consists of one σ(p) bond and two (formal) half π bonds.

3.7. $c\,^1\Pi$

From Fig. 1 the asymptotic fragments of the $c\,^1\Pi$ state are N(^{2}P) + Li(^{2}S), or schematically as in Scheme 5. The above picture suggests that the two



Scheme 4.

atoms are held together by a formal half σ bond. On the other hand from Table 1 we can see that we are dealing with a rather strong (internal bond strength 50.0 kcal mol^{-1}), short bond. This could mean that there is an avoided crossing between this state and the $d\,^1\Pi$ state (see below). As was mentioned before, due to an overestimation of the $\Delta E(^2P \leftarrow {}^4S;\ N)$ splitting, the entire $c\,^1\Pi$ curve should be upshifted by 13.4 kcal mol^{-1}, therefore increasing the calculated T_e value by an equal amount, $T_e \cong 61.0$ kcal mol^{-1}.

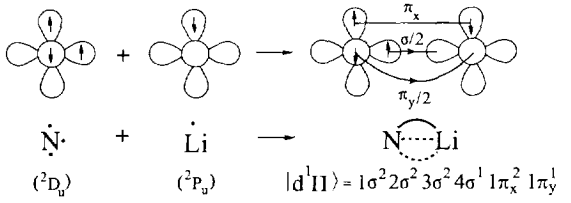
3.8. $C\,^3\Pi$

This state has the same asymptotes as those of the $c\,^1\Pi$ state, Fig. 1, but the two electrons are coupled into a triplet: $C\,^3\Pi = 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_x^1 1\pi_y^1 \alpha\alpha$. With all the reservations suggested by the unnatural potential energy curve of Fig. 1, we calculate an internal bond strength of ≈ 16.0 kcal mol^{-1} and a very large bond distance. With such a potential curve the $R_{N-Li} \cong 3.0$ Å presented in Table 1 cannot be taken very seriously. Our T_e value corrected by 13.4 kcal mol^{-1} is ≈ 92.0 kcal mol^{-1} in relatively good agreement with the corresponding value of Ref. [5], 100 kcal mol^{-1}.

3.9. $d\,^1\Pi$

This state originates from the first excited states ^{2}D and ^{2}P of N and Li atoms respectively, Fig. 1, see Scheme 6. Remember that the $\Delta E(^2D \leftarrow {}^4S;\ N)$ is overestimated by 3.6 kcal mol^{-1} (see state $a\,^1\Delta$, 3.4) therefore the whole potential curve should be shifted by an equal amount rendering the T_e value ≈ 112 kcal mol^{-1}, Table 1.

The bonding scheme, according to the previous icon, can be thought of as comprised of a π bond, a half σ bond and a half π bond. The binding mode is identical with that of the $A\,^3\Pi$ (3.2) state as it can be



Scheme 6.

seen from the corresponding inset (Scheme 2). Nevertheless the predicted bond length of the $d^1\Pi$ is very large, being ≈ 3.4 Å, while that of $A^3\Pi$ is 1.772 Å. In addition the internal bond strength of the $d^1\Pi$ state is only 9 kcal mol^{-1} as compared with the 64.6 kcal mol^{-1} bond strength of the $A^3\Pi$ state, Table 1. These seemingly conflicting observations as well as the irregular shape of the $d^1\Pi$ curve, can be accounted by an avoided crossing between the $c^1\Pi$ and the $d^1\Pi$ states. This assumption is enforced by observing that the bond length of the $c^1\Pi$ is practically the same as that of $A^3\Pi$ despite the apparently different mode of bonding between these two states.

4. Concluding remarks

(1) The ground state of the NLi molecular system is of $^3\Sigma^-$ symmetry with a dissociation energy $D_e = 29.5$ (32) kcal mol^{-1} at the MR-CISD (MR-CISD + DV) level. The bonding is very ionic, with more than 0.5 electrons transferred from Li to N.

(2) The first excited $A^3\Pi$ state of NLi lies only 7.5 kcal mol^{-1} above the $X^3\Sigma^-$ state, has an internal bond strength of 65 kcal mol^{-1} with respect to the adiabatic fragments N(^{4}S) and Li(^{2}P), and a bond length by 0.15 Å shorter than that of the $X^3\Sigma^-$ state. Both $X^3\Sigma^-$ and $A^3\Pi$ states are equally ionic but the bonding of the latter can be attributed, at least formally, to one and a half π bonds and a half σ bond, as compared to a single σ bond of the former.

(3) By employing valence bond–Lewis icons we can get an intuitive (chemical) understanding of the binding modes for almost all the states described here. Notwithstanding the naiveté of these pictures, we believe there is some benefit to chemists if used appropriately.

(4) Our results for the $X^3\Sigma^-$ and $A^3\Sigma$ states are in qualitative agreement with the results of Dykstra et al. [3], while the differences are due to the much greater correlation recovered in the present work. The differences that are observed between our work and the work of Boldyrev et al. [5], are probably due to the completely different methodologies used by each group: MP2/QCISD(T), single reference calculations versus MR-CISD.

(5) Finally, for pedagogical reasons, it is interesting to note the ability of a typical 'monovalent' atom as Li, to form multiple (traditional) bonds, as for example in states $A^3\Pi$, $B^3\Sigma^-$ and $d^1\Pi$.

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