# Elucidation of the structural characteristics of the isovalent species Li[CO] and Li[CS] by ab initio calculations

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## Abstract

We have performed ab initio CISD(+corrections) calculations on the valence isoelectronic molecules Li[CO] and Li[CS] using large basis sets. The Li–CO, Li–OC, Li–CS and Li–SC $^2\Pi$ states are bound with respect to Li $^2$P by 38, 8, 70 and 41 kcal/mol, respectively. With the exception of LiCS $^2\Sigma^+$, which presents a shallow minimum of 4 kcal/mol, all the relevant $^2\Sigma^+$ states examined are repulsive. Full potential energy curves are also presented for the most interesting of the states.

## 1. Introduction

The field of carbonyl compounds, particularly with transition metal elements, comprises one of the most extended and prolific areas of inorganic and organometallic chemistry [1–3]. The same cannot be said for the carbonyl chemistry of alkali metals where the number of studies, either experimental or theoretical, are limited [4].

This Letter deals with the electronic structure elucidation by ab initio methods of the simplest alkali metal complexes, namely, monolithium carbonyl, Li[CO] and monolithium thiocarbonyl, Li[CS]. Concerning the latter and to the best of our knowledge no information of any kind exists in the literature.

Relatively recently the interaction of Li with CO has been studied experimentally via matrix isolation vibrational spectroscopy [4,5]. Although the results are not easily interpretable due to complications of

solid noble gas matrices, and to the difficulty of controlling the relative Li-to-CO concentrations, it is clear that Li and CO interact rather strongly, and as far as the Li[CO] complex is concerned a vibrational frequency in the range 610–620 cm$^{-1}$ has been isolated.

At this point it is pertinent to examine the possible modes of interaction of the Li atom with either the CO or CS species (CX, X = O or S). The ground state electronic structure of these isovalent molecules is fairly well represented by the following valence bond-Lewis icon.
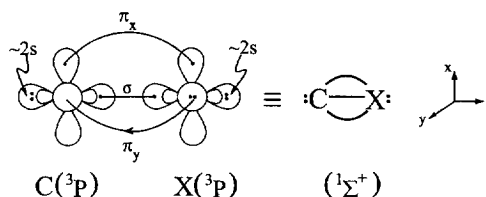


$$C(^3P) \qquad X(^3P) \qquad (^1\Sigma^+)$$

It is reminded that the dipole moment of CO and CS is 0.11 and 1.96 D, respectively [6], with the negative end of the dipole in both species pointing towards the C atom.

Considering a linear geometry, the Li atom can approach either ends of CO or CS. With the CO or CS species always in their ground state, two modes of interaction are obvious.

(a) With the Li atom in its $^2$S ground state

$$:X \quad C: + \cdot Li \rightarrow Li \cdot [:C \quad X:]$$
$$\phantom{:X} {}^1\Sigma^+ \phantom{C: +} {}^2S \phantom{\cdot Li \rightarrow Li \cdot [:C \quad} {}^2\Sigma^+$$

certainly resulting, at least to a first order of approximation, in a Pauli dissociative (repulsive) $^2\Sigma^+$ state.

(b) With the Li atom in its first $^2$P excited state



$$:X\!\!\frown\!\!C: \quad + \quad \dot{Li} \quad \longrightarrow \quad :X\!\!\frown\!\!C\!\!-\!\!Li$$
$$({}^1\Sigma^+) \phantom{xxx} ({}^2P, M_L = \pm 1) \phantom{xxxxx} ({}^2\Pi)$$

anticipating a stable, at least with respect to the $^2$P state of Li, state of $^2\Pi$ symmetry, X   C–Li (or Li–X   C).

From the above considerations it is clear that any interaction in the $^2\Pi$ state between CX and Li would be due to electron transfer along the $\sigma$-frame from the C or X end of the CX molecule towards the $p_\sigma$ empty orbital of the Li atom, with a concomitant "back" electron transfer from the Li $p_\pi$ orbital towards the available $\pi^*$ (antibonding) orbitals of the CX system. Because of the direction and the size of the CX dipole moment we anticipate a stronger interaction from the C rather than the X end of CX and with CS rather than the CO molecule. It is interesting to note at this point that due to the nature of the Li, CX interaction of either $\Sigma$ or $\Pi$ symmetry, even Hartree–Fock (HF) calculations would be size consistent [7], something useful because it allows for the simple construction of full potential energy curves (PECs).

In 1986 Silvi et al. [8] published ab initio calculations on the Li[CO] system using the 4-31G and 6-31G$^*$ bases. They reported geometries of the $^2\Pi$ Li[CO] state at the UHF level of theory and gave partial post-HF/4-31G PECs using the CIPSI approach. No absolute energies were reported and no dissociation energies were given explicitly. The main conclusions were that both the Li–CO and Li–OC $^2\Sigma^+$ states were repulsive, while the $^2\Pi$ Li–CO state was bound with respect to the $^2$P state of Li, lying some 10 or 19 kcal/mol higher at the CI/4-31G or CI/6-31G$^*$ level, respectively, from the asymptotic products of the repulsive $^2\Sigma^+$ state, i.e. Li($^2$S) + CO($^1\Sigma^+$). The other Li–OC $^2\Pi$ state was predicted to be repulsive as well. They also argued that the binding in the Li–CO $^2\Pi$ state could be pictured as a charge transfer complex between Li$^+$ and CO$^-$.

Pullumbi et al. [9] published density functional calculations (DFT) on M–CO (M = Li, Na, K) complexes. Concerning the Li–CO case they concluded that the $^2\Pi$ state was the ground state, located 3.8 kcal/mol *below* the Li($^2$S) + CO($^1\Sigma^+$) ground state products of the $^2\Sigma^+$ state. This would mean a Li–CO *internal bond strength* (with respect to the Li $^2$P state), of 46.5 kcal/mol, assuming that they calculated correctly the 1.85 eV = 42.7 kcal/mol [10] $^2$P ← $^2$S Li atomic energy splitting at the DFT level.

The scarce data on these chemically peculiar species and the above mentioned rather conflicting results, gave us the stimulus to re-examine the electronic structures of the Li[CO] complex, employing large to very large basis sets and standard CISD configuration interaction methods (SCF + single + double replacements + Davidson corrections). In addition, analogous computations are presented for the isovalent to Li[CO], Li[CS] system. It is reminded that for an 11-electron valence system over 90% of the total valence electron correlation can be recovered at the CISD level, as is evidenced from the full-CI Davidson extrapolation formula [11].

## 2. Computational approach

For all atoms the correlation consistent polarized valence Gaussian basis sets (cc-pVXZ) of Dunning [12] were employed. In particular, for the C and O

Table 1
Energies $E$ (hartree), equilibrium bond lengths $r_e$ (Å), Mulliken charges $q$ and dipole moments $\mu$ (D) for different basis sets of CO and CS in their $^1\Sigma^+$ ground states

| Basis set | Method | CO | | | | CS | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $-E$ | $r_e$ | $\mu$ | $q_O$ | $E$ | $r_e$ | $\mu$ | $q_S$ |
| cc-pVDZ | SCF | 112.75052 | 1.113 | −0.157 | −0.08 | | | | |
| | CISD | 113.02859 | 1.134 | +0.170 | 0.0 | | | | |
| | CISD + Q [a] | 113.052 | 1.141 | | | | | | |
| cc-pVTZ | SCF | 112.78001 | 1.105 | −0.173 | −0.28 | 435.35230 | 1.515 | 1.720 | +0.01 |
| | CISD | 113.11131 | 1.121 | +0.076 | −0.18 | 435.63978 | 1.528 | 1.916 | +0.07 |
| | CISD + Q [a] | 113.139 | 1.128 | | | 435.674 | 1.537 | | |
| cc-pVQZ-g [b] | SCF | 112.79031 | 1.103 | −0.142 | −0.18 | 435.35985 | 1.520 | 1.687 | +0.21 |
| | CISD | 113.13707 | 1.119 | +0.097 | −0.09 | 435.65939 | 1.535 | 1.914 | +0.27 |
| | CISD + Q [a] | 113.167 | 1.126 | | | 435.695 | 1.547 | | |
| aug-cc-p VQZ-g [b,c] | SCF | 112.78971 | | | | 435.35963 | | | |
| | CISD | 113.13817 | | | | 435.66042 | | | |
| | CISD + Q [a] | 113.168 | | | | 435.696 | | | |
| | exp. [6] | | 1.1283 | +0.11 | | | 1.5349 | 1.96 | |

[a] Davidson correction for unlinked quadruples, Ref. [11].
[b] cc-p VQZ without g functions.
[c] No geometry optimization, the geometry of cc-pVQZ-g was used.

atoms the cc-pVDZ, cc-pVTZ, cc-pVQZ-g (without g functions) and aug-cc-pVQZ-g (cc-pVQZ-g + diffuse functions) [13] were used, while for the S atom [14] the cc-pVTZ, cc-pVQZ-g and aug-cc-pVQZ-g were used. For the Li the cc-pVDZ, cc-pVTZ and cc-pVQZ-g bases were employed. For

Table 2
Absolute energies $E$ (hartree), bond lengths $r_e$ (Å), dissociation energies $D_e$ (kcal/mol), dipole moments $\mu$ (D) and Mulliken charges $q$ of the $^2\Pi$ state of Li–CO

| Basis set | Method | $-E$ | $r_{Li-CO}$ | $r_{LiC-O}$ | $D_e$ [a] | $\mu$ | $q_{Li}$ | $q_C$ | $q_O$ |
|---|---|---|---|---|---|---|---|---|---|
| cc-pVDZ | SCF | 120.15178 | 1.955 | 1.136 | 23.0 | 4.80 | +0.09 | +0.06 | −0.15 |
| | CISD | 120.44111 | 1.942 | 1.162 | 30.1 | 4.97 | +0.12 | −0.03 | −0.09 |
| | CISD + Q [b] | 120.467 | 1.946 | 1.170 | 31.6 | | | | |
| cc-pVTZ | SCF | 120.18574 | 1.915 | 1.135 | 25.6 | 5.30 | +0.12 | +0.26 | −0.38 |
| | CISD | 120.53199 | 1.894 | 1.157 | 34.9 | 5.53 | +0.16 | +0.13 | −0.29 |
| | CISD + Q [b] | 120.563 | 1.894 | 1.165 | 37.0 | | | | |
| cc-pVQZ-g [c,d] | SCF | 120.19397 | | | 24.2 | 5.96 | +0.10 | +0.27 | −0.37 |
| | CISD | 120.55893 | | | 35.7 | 5.62 | +0.10 | +0.15 | −0.25 |
| | CISD + Q [b] | 120.592 | | | 37.7 | | | | |
| aug-cc-pVQZ-g [c,d] | SCF | 120.19421 | | | 24.8 | | | | |
| | CISD | 120.55935 | | | 35.2 | | | | |
| | CISD + Q [b] | 120.593 | | | 37.6 | | | | |
| 6-31G* [e] | UHF/CIPSI [e] | | 1.931 | 1.144 | bound | 5.11 | +0.20 | +0.19 | −0.38 |
| ~ DZ + P [f] | DFT [f] | 120.80384 | 1.918 | 1.174 | 3.82 [g] | 5.64 | | | |

[a] With respect to Li($^2$P) + CO($^1\Sigma^+$) (internal bond strength).
[b] Davidson correction for unlinked clusters.
[c] cc-pVQZ with the g functions removed.
[d] The cc-pVTZ geometry was used.
[e] Ref. [8].    [f] Ref. [9].
[g] Ref. [9], $D_e$ with respect to Li($^2$S) + CO($^1\Sigma^+$), see text.

Table 3

Absolute energies $E$ (hartree), bond distances $r_e$ (Å), dissociation energies $D_e$ (kcal/mol), dipole moments $\mu$ (D) and Mulliken charges $q$ of the $^2\Pi$ state of Li–OC

| Basis set | Method | $-E$ | $r_{\text{Li-OC}}$ | $r_{\text{LiO-C}}$ | $D_e$ [a] | $\mu$ | $q_{\text{Li}}$ | $q_{\text{C}}$ | $q_{\text{O}}$ |
|---|---|---|---|---|---|---|---|---|---|
| cc-pVDZ | SCF | 120.12566 | 2.071 | 1.117 | 6.6 | 1.13 | −0.07 | +0.19 | −0.12 |
| | CISD | 120.40599 | 2.021 | 1.142 | 8.0 | 0.70 | −0.08 | +0.12 | −0.04 |
| | CISD + Q [b] | 120.430 | 2.021 | 1.142 | 8.4 | | | | |
| cc-pVTZ | SCF | 120.15361 | 2.041 | 1.109 | 5.4 | 1.28 | −0.07 | +0.44 | −0.37 |
| | CISD | 120.48703 | 1.999 | 1.129 | 6.7 | 0.98 | −0.08 | +0.36 | −0.28 |
| | CISD + Q [b] | 120.516 | 1.970 | 1.137 | 7.5 | | | | |
| cc-pVQZ-g [c] | SCF | 120.16288 | | | 4.7 | 1.45 | 0.0 | +0.43 | −0.43 |
| | CISD | 120.51391 | | | 7.4 | 1.01 | −0.01 | +0.33 | −0.32 |
| | CISD + Q [b] | 120.544 | | | 7.6 | | | | |
| 4-31G [d] | CIPSI | | | | repulsive | | | | |

[a] With respect to Li($^2$P) + CO($^1\Sigma^+$).

[b] Davidson correction.

[c] cc-pVQZ with the g functions removed, geometries of the cc-pVTZ basis.

[d] Ref. [8].

example, our largest basis set for the Li[CO] with diffuse functions on the C and O atoms is (12s6p3d2f/13s7p4d3f/13s7p4d3f) generally con-tracted [15] to [5s4p3d2f/6s5p4d3f/6s5p4d3f], con-sisting of 170 spherical Gaussians. The main advan-tages of the cc-pVXZ basis sets are the systematic

Table 4

Absolute energies $E$ (hartree), bond distances $r_e$ (Å), dissociation energies $D_e$ (kcal/mol), dipole moments $\mu$ (D), and Mulliken charges $q$ of the $^2\Pi$ states of Li–CS and Li–SC

| Basis set | Method | Li–CS ($^2\Pi$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $-E$ | $r_{\text{Li-CS}}$ | $r_{\text{LiC-S}}$ | $D_e$ [a] | $\mu$ | $q_{\text{Li}}$ | $q_{\text{C}}$ | $q_{\text{S}}$ |
| cc-pVTZ | SCF | 442.81236 | 1.899 | 1.565 | 59.7 | 7.88 | +0.38 | −0.15 | −0.23 |
| | CISD | 443.11240 | 1.889 | 1.568 | 67.5 | 7.44 | +0.36 | −0.22 | −0.14 |
| | CISD + Q [b] | 443.147 | 1.886 | 1.575 | 68.0 | | | | |
| cc-pVQZ-g [c] | SCF | 442.81963 | | | 59.4 | 7.9 | +0.48 | −0.48 | 0.0 |
| | CISD | 443.13423 | | | 68.9 | 7.5 | +0.47 | −0.52 | +0.05 |
| | CISD + Q [b] | 443.171 | | | 69.6 | | | | |
| aug-cc-pVQZ-g [c] | SCF | 442.81981 | | | 59.7 | | | | |
| | CISD | 443.13443 | | | 68.4 | | | | |
| | CISD + Q [b] | 443.172 | | | 69.6 | | | | |
| | | Li–SC ($^2\Pi$) | | | | | | | |
| | | | $r_{\text{Li-SC}}$ | $r_{\text{LiS-C}}$ | | | | | |
| cc-pVTZ | SCF | 442.77306 | 2.110 | 1.658 | 35.0 | 9.60 | +0.30 | −0.05 | −0.25 |
| | CISD | 443.06626 | 2.121 | 1.637 | 38.6 | 9.86 | +0.30 | −0.15 | −0.15 |
| | CISD + Q [b] | 443.101 | 2.127 | 1.640 | 39.2 | | | | |
| cc-pVQZ-g [c] | SCF | 442.77981 | | | 34.5 | 9.80 | +0.52 | −0.40 | −0.12 |
| | CISD | 443.08777 | | | 39.8 | 9.97 | +0.50 | −0.41 | −0.09 |
| | CISD + Q [b] | 443.125 | | | 40.8 | | | | |

[a] With respect to Li($^2$P) and CS($^1\Sigma^+$). For Li–CS the binding energy with respect to Li($^2$S) is obtained by subtracting 1.85 eV = 42.7 kcal/mol.

[b] Davidson correction

[c] cc-pVQZ with the g functions removed, geometries of the cc-pVTZ basis.
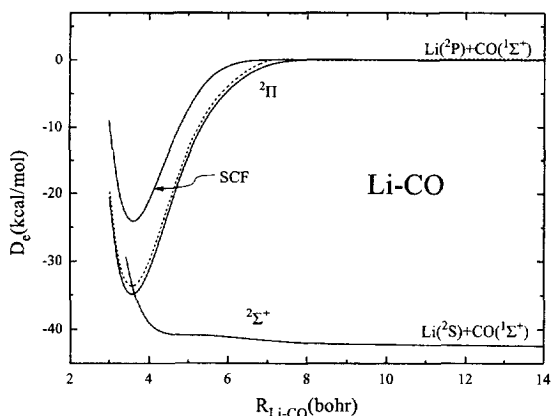
Fig. 1. Potential energy curves of the Li–CO $^2\Sigma^+$ and $^2\Pi$ states at the SCF and CISD/cc-pVQZ-g levels. The dashed curve is at the CISD/cc-pVTZ level.
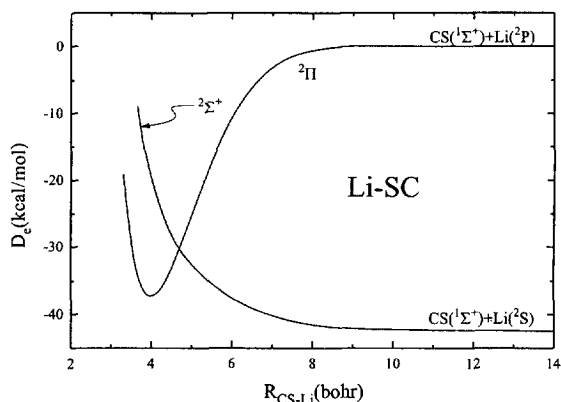


Fig. 3. Potential energy curves of the Li–SC $^2\Pi$ and $^2\Sigma^+$ states at the SCF and CISD/cc-pVQZ-g level.

improvement of the atomic energies as a "function" of X [12] and that they provide the lowest possible CISD energies for the given basis set size [14]. In all correlated calculations the $\sim 1s^2$ electrons of the Li, C and O, and the $\sim 1s^2 2s^2 2p^6$ electrons of S were kept frozen at the SCF level.

The computational method employed in the present study is CISD ( + Davidson corrections). Full energy potential curves were constructed for both species Li[CO] and Li[CS] in their linear configurations; no bent geometries were examined. The computations were performed with the programs MELD

[16] and COLUMBUS [17] with all reported properties calculated by the MELD suite of codes. Spectroscopic constants $\omega_e$, $\omega_e \chi_e$ and $\alpha_e$ were calculated by considering the –CX moiety as a point mass, fitting the corresponding PEC up to $\approx 5.5$ bohr to a seventh degree polynomial and applying a standard Dunham analysis.

## 3. Results and discussion

At the cc-pVDZ, cc-pVTZ and cc-pVQZ-g levels the absolute energies of Li($^2$S) and the Li($^2$P $\leftarrow ^2$S)
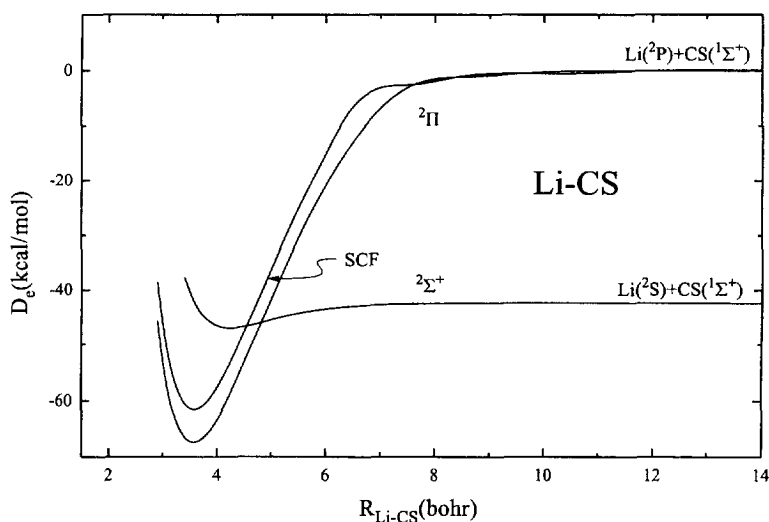


Fig. 2. Potential energy curves of the Li–CS $^2\Pi$ and $^2\Sigma^+$ states at the SCF and CISD/cc-pVTZ levels of theory.

energy splittings are $-7.43242$, $-7.43268$, $-7.43269$ hartree and 1.85, 1.84, 1.84 eV respectively, with the experimental value of the latter being 1.85 eV [10]. Table 1 summarizes the energy values, equilibrium bond lengths, Mulliken charges and dipole moments of the free CO and CS molecules as a function of basis set size. Tables 2, 3 and 4 present results of the $^2\Pi$ states of Li–CO, Li–OC, Li–CS and Li–SC in different basis sets at the SCF, CISD and CISD + Q levels of theory. For the $^2\Pi$ and $^2\Sigma^+$ states of Li–CO, Li–CS and Li–SC full PECs are presented in Figs. 1, 2 and 3. Finally, spectroscopic constants are reported in Table 5.

*Li–CO, $^2\Pi$.* From Table 2 it is observed that the Li–CO binding energy $D_e$ with respect to the $^2P$ state of Li (*internal bond strength*) is 35.7 kcal/mol at the CISD/cc-pVQZ-g (37.7 kcal/mol at the CISD + Q) level. The convergence of the $D_e$ values with respect to the basis set size, and the indicative values of the +Q Davidson correction, supports that an $\approx 38$ kcal/mol Li–CO $D_e$ value can be considered as final, thus this state lies $\approx 4.5$ kcal/mol *higher* than the ground state products Li($^2S$) + CO($^1\Sigma^+$) of the $^2\Sigma^+$ dissociative state, Fig. 1. This should be contrasted with the results of Pullumbi et al. [9], who at the DFT level calculated that the Li–CO $^2\Pi$ state is 3.8 kcal/mol *lower* than the ground state products. On the other hand, our results are in qualitative agreement with the results of Silvi et al. [8], but no $D_e$ value is given explicitly by these workers. The Li–CO and LiC–O geometries presented here differ from those reported in Refs. [8,9], the largest difference being 0.04 Å in the Li–CO distance, Table 2.

The elongation of the LiC–O bond by 0.036 Å (CISD/cc-pVTZ) with respect to the free CO (Table 1) supports our population analysis of approximately $0.2e^-$ being transferred from Li to the $\pi^*$ orbitals of CO, Table 2.

Notwithstanding the pitfalls of the Mulliken population analysis a more detailed approach reveals that at equilibrium, the Li atom gains via the σ-frame $\approx 0.4e^-$, losing at the same time via the $\pi_x$-frame $\approx 0.6e^-$, or that the in situ Li atom has the distribution $\sim p_x^{0.4} p_y^{0.0} p_z^{0.4}$. The C atom loses via the σ-frame $\approx 0.7e^-$ gaining at the same time $\approx 0.6e^-$ via the $\pi_y$-frame. Finally, the O atom gains via the σ-frame $\approx 0.25e^-$, via the $\pi_x$-frame $0.6e^-$, while losing at the same time via the $\pi_y$-frame $\approx 0.6e^-$.

*Li–OC, $^2\Pi$.* Table 3 shows that the Li–OC $D_e$ with respect to the Li $^2P$ state (internal bond strength) is not larger than 8 kcal/mol and is practically constant in all basis sets used. As expected, due to the small binding interaction the Li–OC bond is quite long, $r_e = 2.00$ Å, while the LiO–C bond lengthens by less than 0.01 Å as compared to the free CO at the CISD/cc-pVTZ level. Nevertheless, the presence of the Li atom, although itself remaining essentially neutral, induces a large charge redistribution in the –OC moiety and as a result the Li–OC system acquires a dipole moment of $\approx 1$ D. Notice that Silvi et al. [8] predict a repulsive Li–OC $^2\Pi$ state.

*Li–CS, $^2\Pi$.* From Table 4 we observe that the $^2\Pi$ is the ground state of the Li–CS system with a $D_e$ (internal bond strength) of 68.9 kcal/mol at the CISD/cc-pVQZ-g level (70 at the +Q level); there-

Table 5
Spectroscopic constants, $\omega_e$, $\omega_e \chi_e$ and $\alpha_e$ in cm$^{-1}$ of the $^2\Pi$ states of Li–CO, Li–CS and Li–SC at the CISD level of theory [a]

| Basis set | Li–CO | | | Li–CS | | | Li–SC | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\omega_e$ | $\omega_e \chi_e$ | $\alpha_e$ | $\omega_e$ | $\omega_e \chi_e$ | $\alpha_e$ | $\omega_e$ | $\omega_e \chi_e$ | $\alpha_e$ |
| cc-pVTZ | 640.8 | 5.8 | 0.01 | 632.9 | 3.1 | 0.009 | 551.6 | 1.8 | 0.007 |
| cc-pVQZ-g | 635.1 | 4.6 | 0.01 | | | | | | |
| Exp. [b] | 610–620 | | | | | | | | |

[a] The –CO and –CS moieties were considered as single point masses with $^7$Li–CO and $^7$Li[CS] reduced masses $\mu = 5.610000$ and 6.050593, respectively.
[b] Ref. [4].

fore, with a binding energy of 26.2 kcal/mol with respect to the *ground* state products, $Li(^2S) + CS(^1\Sigma^+)$, Fig. 2. As the population analysis indicates $\approx 0.5e^-$ are transferred from $Li(^2P)$ to CS, thus causing the energy to plummet some 26 kcal/mol below the $^2\Sigma^+$ asymptotic products, Fig. 2. At the cc-pVTZ basis a more detailed population analysis reveals that the $Li(^2P)$ atom gains $\approx 0.48e^-$ via the $\sigma$-frame losing at the same time $\approx 0.83e^-$ via the $\pi_x$-frame, so the in situ Li can be written as $\sim p_x^{0.17}p_y^{0.0}p_z^{0.48}$. The C atom via the $\sigma$-frame loses $\approx 0.47e^-$ (they are moving towards the $p_z$ of Li), while via the $\pi_y$-frame, gains $\approx 0.63e^-$. The S atom gains $\approx 0.76e^-$ via the $\pi_x$-frame losing at the same time $\approx 0.66e^-$ via the $\pi_y$-frame. The binding mechanism is mutatis-mutandis similar to that of Li–CO ($^2\Pi$), i.e. $\sigma$-donation and $\pi$-backdonation, but the Li atom loses $\approx 0.5e^-$ as compared to $0.1e^-$ in LiCO with a different charge distribution in the –CS moiety as compared to the –CO moiety. The much higher polarity of LiCS is also reflected in its larger dipole moment as compared to LiCO, $\Delta\mu \approx 2$ D. Similarly, as in LiC–O, the LiC–S bond length increases by $\approx 0.05$ Å compared to free CS, Table 1.

*Li–SC, $^2\Pi$.* Despite the formal similarities between Li–SC and Li–OC the two systems present remarkable differences. (a) Li–SC has a dissociation energy $D_e$ with respect to $Li(^2P)$ (internal bond strength), of 39.8 kcal/mol at the CISD/cc-pVQZ-g, Table 4. This should be contrasted to 7.4 kcal/mol for Li–OC at the same level of theory. Assuming that the Davidson correction points towards the correct direction, this $^2\Pi$ state is just $\approx 2$ kcal/mol above the asymptotic products of the repulsive $^2\Sigma^+$ (ground) state, Fig. 3. (b) The LiSC molecule has a high dipole moment, $\mu = 10$ D, higher by 2.5 D from the Li–CS dipole moment. Notice that the $\mu$ value of Li–OC is 1 D, Table 3. (c) The bond distance LiS–C is lengthened by 0.112 Å as compared to the free CS at the CISD/cc-pVTZ level, while the corresponding number between LiO–C and CO is 0.008 Å.

For the cc-pVTZ basis the population analysis reveals that $0.3e^-$ (0.5 at the cc-pVQZ-g) are transferred from Li– to –SC equally distributed between the in situ atoms S and C. In detail, Li gains $\approx 0.4$ and $\approx 0.1e^-$ via the $\sigma$- and $\pi_y$-frames, losing at the

same time $\approx 0.8e^-$ via the $\pi_x$-frame, or $\sim p_x^{0.2}p_y^{0.1}p_z^{0.4}$. The C atom loses $\approx 0.27e^-$ via the $\sigma$-frame, gaining $\approx 0.40e^-$ via the $\pi_y$-frame. Finally, S is losing $\approx 0.14$ and $0.5e^-$ via the $\sigma$- and $\pi_y$-frames, respectively, gaining $0.75e^-$ via the $\pi_x$-frame.

Table 5 presents the spectroscopic constants $\omega_e$, $\omega_e \chi_e$ and $\alpha_e$ of the Li–CO, Li–CS and Li–SC $^2\Pi$ states. Our $\omega_e$ value of 635 cm$^{-1}$ for Li–CO, at the CISD/cc-pVQZ-g level, is in fair agreement with the experimental value [4] of 610–620 cm$^{-1}$.

*The $^2\Sigma^+$ states.* All the $^2\Sigma^+$ states of both molecules, i.e. Li–CO, Li–OC, Li–CS and Li–SC correlate with the ground states $Li(^2S) + CO$ or $CS(^1\Sigma^+)$; the Li–CO, Li–OC and Li–SC $^2\Sigma^+$ states are repulsive. Figs. 1 and 3 show the repulsive PECs of the Li–CO and Li–SC species. The Li–CS $^2\Sigma^+$ presents a shallow minimum of 4.2 kcal/mol at the CISD/cc-pVTZ level (3.1 kcal/mol at the SCF and 5.1 kcal/mol at the CISD + Q), with the following equilibrium geometry: $r_{Li-CS} = 2.25$ Å and $r_{LiC-S} = 1.512$ Å; the corresponding PEC is shown in Fig. 2.

## 4. Concluding remarks

In the present study we have examined at the CISD + Q level of theory and using different basis sets of cc-pVXZ [12] quality (X = D, T, Q) the $^2\Pi$ and $^2\Sigma^+$ states of the isovalent complexes Li[CO] and Li[CS]. No bent (Renner–Teller) states have been examined. Our main conclusions are:

(1) The Li–CO and Li–CS $^2\Pi$ states are bound by 38 and 70 kcal/mol respectively with respect to the $Li(^2P) + CX(^1\Sigma^+)$ states, which means that Li–CO is *unbound* with respect to the ground state products by $\approx 5$ kcal/mol, while the Li–CS is bound with a dissociation energy of $\approx 27$ kcal/mol.

(2) The Li–OC and Li–SC $^2\Pi$ states are bound by $\approx 8$ and $\approx 40$ kcal/mol with respect to the $Li(^2P) + CX(^1\Sigma^+)$ states. In addition, the Li–SC species has a remarkably high dipole moment $\mu = 10$ D. Just for comparative purposes we mention that LiBr, an essentially ionic molecule with bond length similar to that of Li–SC ($r_{LiBr} = 2.17$ Å), has a dipole moment $\mu = 7.3$ D [6].

(3) With the exception of Li–CS $^2\Sigma^+$ which in

the PEC shows a shallow minimum of $\approx 4 \text{ kcal/mol}$, the rest of the $^2\Sigma^+$ states, i.e. Li–CO, Li–OC and Li–SC are clearly repulsive.

(4) The binding of the $^2\Pi$ symmetry species Li–CO, Li–CS and Li–SC can be rationalized to a synergistic $\sigma$-electron transfer towards Li with a synchronous back-transfer towards CX. The net result is an always in situ positively charged Li atom. Some understanding of the large difference in binding energies between the two $^2\Pi$ pairs (Li–CO, Li–CS) and (Li–OC, Li–SC), $\approx 32 \text{ kcal/mol}$, can be gleaned by considering the energies of the $\pi^*$ orbitals of the free CO and CS species. For the cc-pVTZ basis the corresponding numbers are $+3.90$ and $+1.66$ eV, thus rendering the $\pi^*$ system of CO less available than that of CS, thus $\approx 0.3e^-$ more are transferred to the [CS] as compared to the [CO] moiety.

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