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An ab initio study of $\text{Li}^+ \cdots \text{C}\equiv\text{S}$, a purely electrostatic system

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Abstract

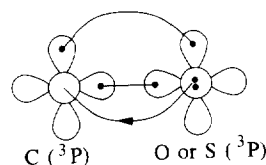
The $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ interaction has been computed by SCF and CISD methods, and it was found to be purely electrostatic with a binding energy D_e of 33 kcal mol^{-1} and a bond distance $R_{\text{Li}^+-\text{C}} = 2.107 \text{ \AA}$.

1. Introduction

The role of electrostatics in the formation of molecules of the ion–dipole type has been pointed out in many theoretical works [1–4]. In the case of a pure electrostatic interaction which is often strong enough to be considered as a bona fide chemical bond, some special characteristics are observed such as large bond lengths, negligible electron transfer, long-tailed coulombic dissociation curves and correct dissociative behaviour, i.e. size consistency, at the, for example, SCF level of theory. It seems that in these cases direct electron transfer is not favoured energetically and, as a consequence, back-donating mechanisms are essentially shut off.

Although the traditional Dewar–Chatt [5] mechanism is largely employed to interpret the bonding in, for example, $\text{M}(\text{CO})_x$ and $\text{M}(\text{CS})_x$ complexes where M is a transition metal element, for M^+-CO systems it was shown by several authors that the metal cation–CO bond bears a predominant electrostatic character [2,4] and has been recently dubbed “non-classical” [6].

It is well known that CO possesses a small dipole moment, $\mu = 0.122 \text{ D}$, with the negative end being at the carbon atom, $\delta^-:\text{C}\equiv\text{O}:\delta^+$ [7]. This, contrary to the usual electronegativity concept result, is pictorially “explained” by the following valence-bond icon



Form 1.

where, clearly, due to the empty π^* orbital of the $\text{C}(^3\text{P})$ atom the in situ electronegativity value of this atom becomes approximately equal to that of the $\text{O}(^3\text{P})$ atom. A metal cation approaching the CO molecule from the C side will interact electrostatically, the strength of the interaction close to equilibrium depending on the detailed electronic distribution of the cation [2].

The isovalent to CO thiocarbonyl system, CS, has an identical ground state structure with that of the CO system, although, contrary to CO, it is

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extremely reactive [8]. Due to the much lower electronegativity of the S atom compared with the O atom the electron transfer from the sulphur to the carbon in the CS($X^1\Sigma^+$) system is much more pronounced, culminating to a large dipole moment, $\mu = 1.958$ D [7], and of course, with the C end of the molecule strongly negatively charged (see below).

The present work examines by ab initio quantum mechanical methods the interaction of the CS system with the simplest metal cation possible, Li^+ . To the best of our knowledge no experimental or theoretical results are available in the literature for this system. The aim of the present study is to show that the $Li^+ \cdots C\equiv S$ interaction is almost entirely of electrostatic nature and to calculate the $(Li-CS)^+$ dissociation energy D_e . Our expectations are based on the large polarity and "softness" of the CS molecule, the energetically unavailable 2s orbital of Li^+ ($\Delta E(1S - 3S) \approx 6$ eV [9]) and the impossibility of any back-donation from Li^+ to CS.

2. Computational details

We have constructed complete SCF and valence CISD, CISD + Davidson correction [10] potential energy curves. The basis sets used are as follows: for the S atom the McLean–Chandler basis [11] 12s10p contracted to 6s5p, for the C and Li atoms, the Dunning [12] 10s6p and 10s bases contracted to 5s4p and 4s respectively. These basis sets were augmented by polarization functions with exponents $\zeta_d(S) = 0.57$ and 2.22.

$\zeta_d(C) = 0.22$ and 0.80 and $\zeta_p(Li^+) = 0.63$. The overall basis set (12s10p2d|10s6p2d|10s1p) \rightarrow [6s5p2d|5s4p2d|4s1p] contains 69 contracted cartesian gaussian functions.

Only linear geometries were optimized using a two-dimensional grid of points around the equilibrium geometry.

Dipole, quadrupole and octopole moments of the CS molecule were obtained as expectation values of the corresponding operators, while the dipole polarizability α_{zz} was extracted by perturbing the CS molecule by an external electric field.

For the $Li^+ \cdots CS$ interaction approximate spectroscopic constants ω_e and $\omega_e x_e$ were obtained by considering the CS moiety as a single mass.

All computations were carried out using the GAMESS [13] and MELD [14] series of codes on a microVAX-3300 computer of the Physical Chemistry Laboratory.

3. Results and discussion

Calculated properties at the SCF and CISD level of the CS ($X^1\Sigma^+$) molecule along with experimental results are shown in Table 1. It is clear that our CISD numbers are in fair agreement with experiment, at least for the purpose of this study. For the Li atom the calculated first ionization potential (or electron affinity of Li^+) is 5.3 eV, in perfect agreement with the experimental value [9].

We have examined the two possible linear geometrical approaches of the Li^+ cation towards

Table 1

Absolute energy E (E_h), equilibrium bond length R_e (\AA), dipole moment μ (D), net Mulliken charge q and dissociation energy D_e (kcal mol^{-1}) of the CS molecule in the ground $X^1\Sigma^+$ state

Method	E	R_e	μ	q_C	D_e
SCF	-435.34889	1.512	1.716	-0.25	103.6
CISD	-435.60874	1.522	2.110	-0.32	142.1
CI-Q ^a	-435.6382	1.529	-	-	154.0
F-CI ^d	-435.6467	1.533	-	-	159.0
Exp. ^b		1.535	1.958		171.3

^a Davidson corrections for unlinked quadruples (CI-Q) and full CI limit (F-CI). Ref. [10].

^b Ref. [7].

the CS molecule, namely $\text{Li}^+ \rightarrow \text{C}\equiv\text{S}$ and $\text{C}\equiv\text{S} \leftarrow \text{Li}^+$. The latter was expected to be repulsive, or at least an energy barrier was expected before any attractive interaction if any. In both cases, bending the triatomic molecular system does not lead to an energy minimum.

Fig. 1 displays potential energy curves at the SCF, SDCI and SDCI+("full CI" Davidson corrections, F-CI) levels of theory, with C and S net Mulliken charge curves shown in the inset. The curves were obtained keeping the $\text{C}\equiv\text{S}$ bond length at the SCF and CISD equilibrium values respectively (Table 1). Completely optimized results on the bond lengths are reported in Table 2.

From Fig. 1 we can see that all three curves are very similar leading to approximately the same $\text{Li}^+ - \text{C}$ bond length of approx. 2.11 Å. The SCF

binding energy and $\text{Li}^+ - \text{C}$ distance does not differ significantly from the corresponding CISD and CISD+correction values. This in turn means that no major changes of the electron correlation occur during the $\text{Li}^+ - \text{CS}$ "bond" formation.

Optimizing the $\text{C}\equiv\text{S}$ bond length in the presence of Li^+ it was found that it contracts by approx. 0.025 Å at all levels of theory with respect to the free $\text{C}\equiv\text{S}$, Table 2.

Fig. 1 shows that the $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ interaction fades out very slowly; at 20 bohr we still have an interaction energy of about $1.3 \text{ kcal mol}^{-1}$, a strong indication that we are dealing with an electrostatic interaction. This evidence is corroborated by the curves in the inset of Fig. 1 showing the net Mulliken charges on C and S: they are perfectly symmetric suggesting that no electron transfer to the Li^+ cation takes place at any distance. At

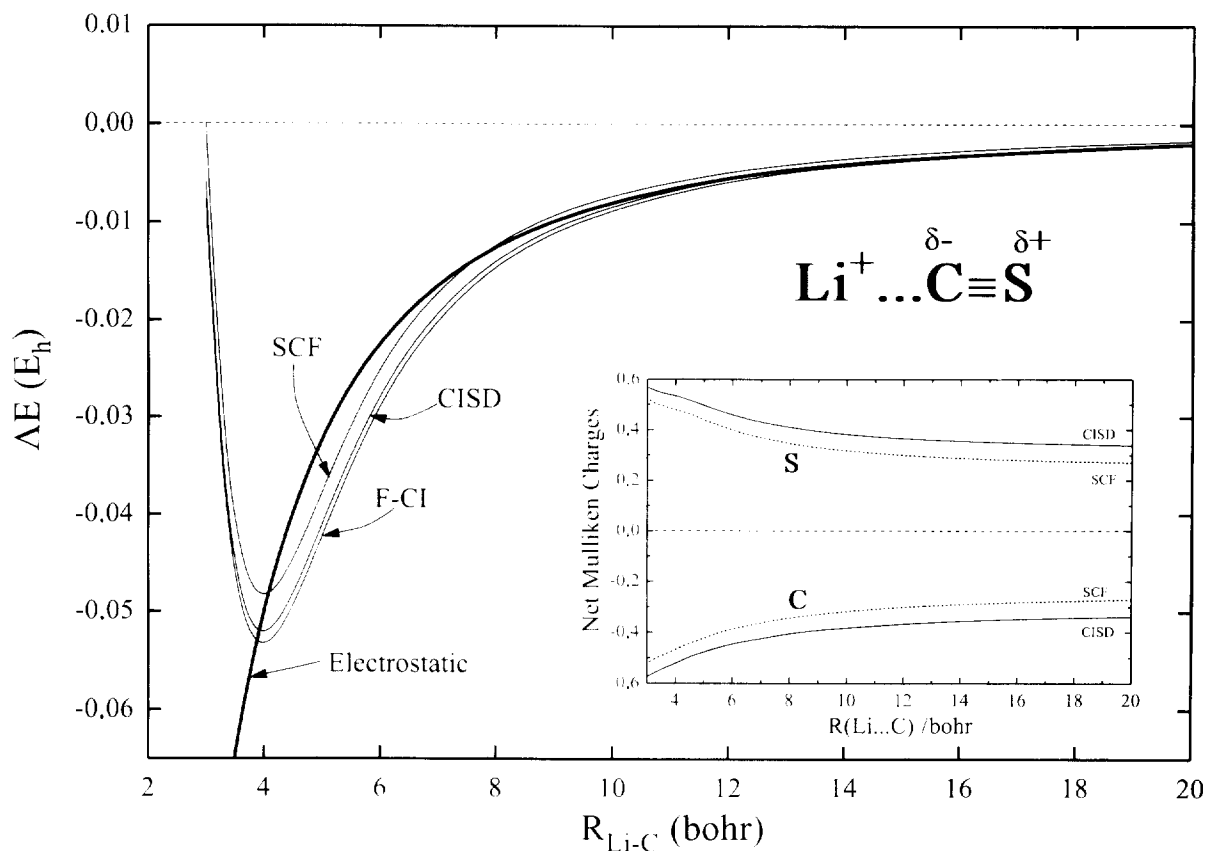


Fig. 1. SCF, CISD and F-CI potential energy curves of the $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ system; the heavy line represents the pure electrostatic interaction, while the inset shows SCF and CISD net Mulliken charges of the C and S atoms as a function of reaction coordinate.

Table 2

Absolute energy E (E_h), equilibrium bond length R_e (Å), harmonic frequency ω_e (cm^{-1}), anharmonicity constant $\omega_e\chi_e$ (cm^{-1}), net Mulliken charge q and dissociation energy D_e (kcal mol^{-1}) for the system $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ at the SCF and CISD levels of theory

Method	E	$R_e(\text{Li}-\text{C})$	$R_e(\text{C}\equiv\text{S})$	$\omega_e(\text{Li}-\text{CS})$	$\omega_e\chi_e(\text{Li}-\text{CS})$	q_{Li}	q_{C}	$D_e(\text{Li}-\text{CS})$
SCF	-442.63462	2.111	1.485	430.2	5.63	+0.99	-0.47	31.1
CISD	-442.89750	2.107	1.498	433.8	4.99	+0.99	-0.52	33.0
CI-Q ^a	-442.9272	2.108	1.508	—	—	—	—	33.0
F-CI ^a	-442.9363	2.106	1.514	431.5	5.17	—	—	33.5

^a See Table 1.

equilibrium the net Mulliken charge on Li^+ is +0.99, Table 2.

A purely electrostatic interaction ΔE for the linear Li^+ approach to $\text{C}\equiv\text{S}$ is described adequately enough by the following formula:

$$\Delta E = \frac{\mu_z}{R^2} + \frac{\Theta_{zz}}{R^3} - \frac{\Omega_{zzz}}{R^4} - \frac{\alpha_{zz}}{2R^4}$$

where, $\mu_z = 0.83010$, $\Theta_{zz} = -1.87096$ and $\Omega_{zzz} = 9.3993$ a.u. are the ab initio CISD dipole, quadrupole and octopole moment tensor components respectively for the free CS molecule. The value of the dipole polarizability α_{zz} was found to be 34.58 a.u.; R is the distance from the centre of mass of the CS molecule.

It is seen that the electrostatic curve coincides with the ab initio potential energy curves at large distances, while it deviates mildly close to the equilibrium. These deviations, in the region of 4–7 bohr, must be attributed to the fact that our electrostatic formula does not include higher order terms and, of course, to the onset of Pauli effects around these distances.

The above discussion clearly points to a purely electrostatic mode of interaction in the $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ system, with a $D_e = 33.0 \text{ kcal mol}^{-1}$ ($D_0 = D_e - \omega_e/2 = 32.4 \text{ kcal mol}^{-1}$) and a Li^+-C bond distance of 2.11 Å. We also observe the significant $\text{C}\equiv\text{S}$ bond shortening which is caused by the increased induced polarity of the CS molecule in the presence of the Li^+ cation, $q_{\text{C}} = -0.52$ compared with $q_{\text{C}} = -0.32$ of the free CS species, Tables 1 and 2.

Notice that for the relevant electrostatic molecule $\text{Li}^+ \cdots \text{C}\equiv\text{O}$, the binding energy is 6–8 kcal mol^{-1} [15].

Finally, we would like to present some results at the SCF level for the sandwich system $\text{S}\equiv\text{C} \cdots \text{Li}^+ \cdots \text{C}\equiv\text{S}$: keeping the $\text{C}\equiv\text{S}$ bond distance frozen at 1.485 Å, $R_{\text{Li}^+-\text{C}} = 2.148$ Å was obtained with a net binding energy with respect to two $\text{CS}(X^1\Sigma^+)$ plus $\text{Li}^+(^1\text{S})$ fragments of 57 kcal mol^{-1} , approximately twice the SCF D_e value previously reported for a single CS molecule, and an absolute total energy of $-878.02477 E_h$. These findings are consistent with the proposed electrostatic model for the Li^+-CS binding.

Approaching the Li^+ ion from the S end of the CS system, a repulsive potential energy curve is observed at all levels of theory. The reason, of course, is the strong positive polarity of the S-end of the CS species. More specifically, a plateau was observed in the region of 5–8 bohr with a synchronous polarity inversion of the $\text{C}\equiv\text{S}$ molecule. No attractive region was found both at SCF and CISD levels; it seems that although the $\text{C}\equiv\text{S}$ polarity inversion favours a $\text{Li}^+ \cdots \text{S}\equiv\text{C}$ stabilization, this polarity inversion destabilizes the $\text{C}\equiv\text{S}$ molecule and the two effects practically cancel each other.

4. Concluding remarks

The main conclusion of the present study is that the system $\text{Li}^+ \cdots \text{C}\equiv\text{S}$ is bound by 33 kcal mol^{-1} with a *completely electrostatic* binding mode: the potential energy curve of $\text{Li}^+ + \text{C}\equiv\text{S}$ can be thought of as an “ab initio titration curve” between the Lewis acid Li^+ and the Lewis base $:\text{C}\equiv\text{S}$. The pure electrostatic nature of this interaction is in evidence for the following reasons.

- (a) No electron transfer from the $C\equiv S$ species to the Li^+ cation is observed.
- (b) The Li^+-CS bond distance is relatively large.
- (c) The potential energy curve can be fitted accurately enough to an electrostatic formula.
- (d) Perfectly size-consistent potential energy curves to asymptotic distances were obtained by SCF and CISD methods, the asymptotic products being $Li^+(^1S;SCF)+CS(X^1\Sigma^+;SCF)$ and $Li^+(^1S;SCF)+CS(X^1\Sigma^+;CISD)$ respectively. This is only feasible if spin coupling/decoupling phenomena are not entailed along the reaction path.

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