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Single- and double-electron reductions of CO_2 by using superalkalis: An ab initio study

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Abstract

CO_2, a major contributor to global warming, can be balanced by converting it into fuels. The reduction of CO_2 has been difficult due to its extremely high stability. Recently, single-electron reduction of CO_2 by superalkalis has been proposed using quantum chemical methods. Herein, we report a systematic study on the single-reduction of CO_2 by using typical superalkalis. Superalkalis are hypervalent species possessing lower ionization energies than alkali atoms. We have studied the interaction of CO_2 with FLi_2, OLi_3, and NLi_4 superalkalis using ab initio MP2 calculations. We notice that this interaction leads to stable superalkali-CO_2 complexes in which the structure of CO_2 is bent due to electron transfer from superalkalis. This clearly reveals that the CO_2 can successfully be reduced to the CO_2^- anion. It has been also noticed that the size of superalkalis plays a crucial in the single-electron reduction of CO_2. For instance, the binding energy of superalkali-CO_2 complex and charge transfer to CO_2 decreases monotonically with the increase in the size of superalkali. We have also proposed that CO_2 can be further reduced to CO_2^{2-} in case of the anionic complex such as $(FLi_2—CO_2)^-$. Thus, FLi_2 superalkali is also capable of double-electron reduction of CO_2. These findings should provide new insights into CO_2-activation as well as motivate further research in this direction.

KEYWORDS
ab initio calculations, CO_2-activation, CO_2-reduction, electronic properties, superalkalis

1 | INTRODUCTION

Carbon dioxide (CO_2), a strong covalently bonded molecule, is a major contributor to global warming. The conversion of CO_2 to fuels is a crucial step that can positively impact the global carbon balance.[1,2] The major challenge in the recycling of CO_2 into usable fuels is that CO_2 is an extremely stable molecule. To convert CO_2 into fuel, it should be first activated or chemically reduced by some catalysts. Although CO_2 can be reduced either electrochemically in which CO_2 is reduced to CO using electrical energy (such as zinc cathode) or photoelectrochemically in which CO_2 is reduced to CO by incident light. Single-electron reduction of CO_2 to CO_2^- is, however, not feasible experimentally due to large reorganization energy between linear CO_2 molecule and bent CO_2^- anion. Note that the electron affinity of CO_2 is negative, which suggests that CO_2^- is metastable. However, CO_2^- anion can be generated through certain mass spectrometric experiments as suggested by Schröder et al.[3] They noticed that CO_2^- anion, which can be regarded as an activated carbon dioxide unit, in which the C—O bonds are weakened, is more stable in the $^2A_1$ state. The potential energy surface (PES) of the CO_2^- anion, explored by Sommerfeld et al.,[4] has identified three vibronically coupled bound states.

It is not even easy to extract an electron from CO_2 due to its high ionization energy of 13 eV. It has been reported only recently[5] that the oxidation of CO_2 can be possible by using superhalogens. Superhalogens[6] are species whose electron affinity exceeds to those of halogen. The counterparts of superhalogens are superalkalis,[7] which possess lower ionization energy than alkali metals. Superalkalis have been previously employed in the design of supersalts,[8–11] superbases,[12–15] alkalides,[16–18] and so forth. It is, therefore, instructive to observe whether superalkalis can be employed to transfer an electron to CO_2. Recently, the capability of reducing CO_2 by novel superalkalis is proposed by Zhao et al.[19] and subsequently, reported by Park and Meloni.[20] This prompted us to perform a systematic study on the interaction of CO_2 with typical superalkalis, known for decades. We noticed that superalkalis can indeed be used to reduce CO_2 into CO_2^- anion. In addition, we have also shown that FLi_2 superalkali is also capable to reduce CO_2 to CO_2^{2-} anion as well. A thorough understanding of the chemical processes involved in the reduction of carbon

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dioxide (CO_2) is of immense importance in biological, environmental, and industrial processes.[21] As mentioned earlier, the CO_2^- anion is bent, unlike the linear structure of a neutral CO_2 molecule. Therefore, the reduction of CO_2 into CO_2^- results in a change in molecular geometry, which generally requires chemical processes such as electrochemical reduction or photochemical reduction. The present study suggests a simple and catalyst-free method of single-electron reduction of CO_2. This should lead to an efficient approach to control and convert CO_2, which is required for environmental safety. We, therefore, believe that this work should appeal to researchers involved in multidisciplinary sciences and working on the interface of physics, chemistry, and environmental sciences.

2 | COMPUTATIONAL DETAILS

All computations were performed using the second order Møller–Plesset perturbative (MP2) method[22] and 6–311 + G(d) basis set in Gaussian 09 program.[23] The total electronic energy and geometry have been obtained without any symmetry constraints in the potential energy surface. The vibrational analysis has been performed at the same level of theory to ensure that all frequency values are positive, that is, the structures belong to true minima in the potential energy surface. This computational scheme has already been adopted in the previous work of Zhao et al.[19]

To verify the reliability of our computational scheme, we have compared our computed results on CO_2^- with those of available experimental as well as literature values. For instance, our computed bond length and symmetric stretching frequency of CO_2 1.170 Å and 1335 cm^{-1} agree well with corresponding experimental values 1.160 Å[24] and 1333 cm^{-1},[25] respectively. Furthermore, our computed bond length of CO_2^- 1.237 Å approximates the experimental value 1.25 Å[26] better than the high-level CCSD(T) computed value of 1.230 Å.[27] The calculated bond angle of CO_2^- (137°) is in the vicinity of 130° as reported earlier by Raman spectroscopy.[28] Moreover, the computed bond length of LiO and binding energy per atom, 1.715 Å and 3.12 eV, are comparable to experimental bond length 1.688 Å[24] and bond dissociation enthalpy of 3.53 eV (340.5 kJ/mol)[29] of LiO, respectively, measured by spectroscopic methods. This may advocate the validity of our computational scheme as well as the reliability of the results reported herein. Although our computed adiabatic electron affinity of CO_2 is −1.04 eV, which overestimates the magnitude of the experimental value (–0.60 eV) reported by Compton et al.[30] and Knapp et al.[31] Similarly, our computed ionization energy of CO_2 14.32 eV slightly overestimates the ionization energy value of 13.78 eV[32] measured by photoelectron spectroscopy. However, it does not affect our conclusions as electron affinity or ionization energy determination is not our objective.

3 | RESULTS AND DISCUSSION

We have studied the interaction of CO_2 molecule with typical superalkali species such as FLi_2, OLi_3, and NLi_4. The ionization energies of these species are calculated to be 3.85 eV for FLi_2, 3.46 eV for OLi_3, and 3.23 eV for NLi_4, which are smaller than that of Li (~5 eV). The equilibrium structures of superalkali-CO_2 complexes are displayed in Figure 1 along with CO_2^- anion and superalkali cations. The relative energy (ΔE) of superalkali-CO_2 complexes and their isomers are collected in Table 1. In all superalkali-CO_2 complexes, the lowest energy structures are those in which both O atoms of CO_2 interacts with two Li atoms of superalkalis. The bond lengths of Li—O interaction lie between 1.865 Å and 1.892 Å. The low lying isomers of FLi_2-CO_2 and OLi_3-CO_2 are 1.07 eV and 0.40 eV higher in energy in which CO_2 interacts via single O atom as shown in Figure 1. In case of NLi_4—CO_2, there is no competiting isomer obtained in our calculations. In all superalkali-CO_2 complexes, CO_2 moiety becomes bent by an angle 133°and the bond lengths C—O become 1.246 Å. These values are comparable to the bond lengths of 1.237 Å and bond angle of 137° in the CO_2^- anion. This suggests that CO_2 can be activated by interaction with superalkalis.

The binding energy (BE) of superalkali-CO_2 complexes are calculated by using following equations;

$$\mathrm{BE} = E[\mathrm{CO_2}] + E[\mathrm{superalkali}] - E[\mathrm{superalkali}-\mathrm{CO_2}]$$

where $E[.]$ represents total (electronic + zero-point) energy of respective species. The BEs of superalkali-CO_2 complexes are listed in Table 1. The basis set superposition error (BSSE) is not included as it hardly affects our BEs due to sufficiently large size of the basis set. One can note that $BE > 0$ and, therefore, all superalkali-CO_2 complexes are energetically stable against dissociation to CO_2. Since the interaction of CO_2 with superalkalis takes place via Li atoms, we have compared the BE values of superalkali-CO_2 complexes with that of LiO molecule, which is computed as 6.24 eV. This may provide some insights into the relative strength of interaction of CO_2 with superalkalis. Although our computed BEs of superalkali-CO_2 complexes are much smaller than that of LiO molecule, these values are comparable to or larger than the BE of Li_3F_2—CO_2, which is calculated to be in the range 1.10–1.69 eV (106–163 kJ/mol) by Park and Meloni.[20]

Furthermore, the BE of superalkali-CO_2 complexes decreases, $BE(FLi_2-CO_2) > BE(OLi_3-CO_2) > BE(NLi_4-CO_2)$, with the increase in the size of superalkalis ($FLi_2 < OLi_3 < NLi_4$). Thus, the interaction between superalkali and CO_2 becomes slightly weaker with the increase in the size of superalkalis. This can be expected due to the fact that larger superalkalis usually possess more delocalized electron cloud.[9] Therefore, charge transfer from larger superalkali such as NLi_4 is not as much effective as in case of smaller superalkali such as FLi_2.

To elucidate CO_2 reduction, we have computed natural bonding orbital (NBO) charges (Δq) and spin density ($\Delta \rho_s$) located on CO_2 as listed in Table 1. In the lowest energy structures of superalkali-CO_2 complexes, the Δq takes a value of $-0.90e$ for FLi_2, $-0.88e$ for OLi_3, and $-0.85e$ for NLi_4. These Δq values follow the same trend as those of BE values as expected due to the fact that lower Δq value results in the decrease in the

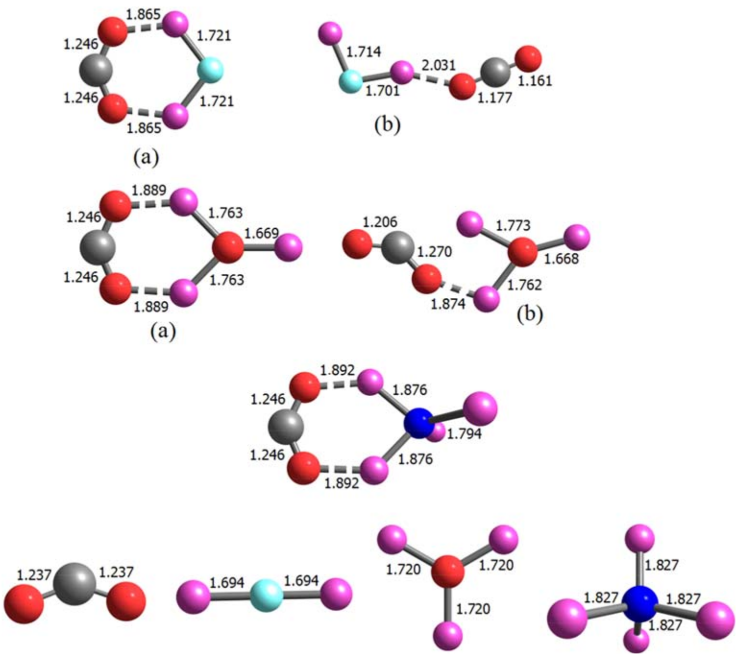

FIGURE 1 Equilibrium structures of superalkali-CO_2complexes with bond lengths in Å. Equilibrium structures of CO_2^- anion, FLi_2^+, OLi_3^+, NLi_4^+superalkali cations are also displayed

strength of charge-transfer interaction. The Δq values have been found to be $-1.26e$ for Al_3—CO_2, $-0.91e$ for $B_9C_3H_{12}$—CO_2, and $-0.63e$ for C_5NH_6 for previously reported complexes by Jena and coworkers.[19] Similarly, the Δq value reported for the most stable structure of F_2Li_3—CO_2 is $-0.78e$,[20] which is smaller than the Δq values presented here. Therefore, the charge transfer from these superalkalis is more effective than that from F_2Li_3 superalkali. In isomer (b) of FLi_2—CO_2, Δq takes very small magnitude ($-0.17e$), which is consistent with almost linear CO_2 moiety just as in neutral CO_2 molecule. On the contrary, the Δq in isomer (b) of OLi_3—CO_2 is, albeit smaller than that in its lowest energy structure (a), large enough to bend CO_2 moiety (see Figure 1). The electron transfer from superalkali to CO_2 in superalkali-CO_2 complexes can also be confirmed by the analysis of the spin density ($\Delta\rho_s$) value. One can note that in the lowest energy structure of all complexes, the $\Delta\rho_s$ becomes 0.96 a.u., which is very close to unity. Thus, the whole spin density (of the unpaired electron) is localized on the CO_2 moiety such that its ground electronic state becomes doublet. In case of FLi_2—CO_2 isomer (b), however, $\Delta\rho_s$ is negligibly small suggesting that the unpaired spin density is localized almost entirely on the FLi_2 superalkali. One may, therefore, assume that the CO_2 moiety exists in its neutral singlet state whereas the FLi_2 superalkali takes its open-shell cationic form.

The singly occupied molecular orbitals (SOMOs) and spin density surfaces are plotted in Figure 2. The SOMOs of FLi_2—CO_2 and OLi_3—CO_2 complexes are localized on CO_2 moiety, which clearly indicates the electron transfer from FLi_2 and OLi_3 superalkali moieties, respectively. In case of NLi_4—CO_2 complex, on the contrary, the SOMO is localized on N atom of NLi_4 superalkali moiety. Although there is indeed an electron transfer from NLi_4 to CO_2, the localization of SOMO is due to the lone pair of nitrogen. This fact is further confirmed by spin density surfaces, which suggest that the spin density is localized on CO_2 moiety due to the unpaired electron for all superalkali-CO_2 complexes studied here. The SOMO eigenvalues of superalkali-CO_2 complexes are also listed in Table 1. One can note that the SOMO energies are fairly large, which suggest that the unpaired electron is strongly bound. However, these SOMO energy values decrease with the increase in the size of the superalkalis, following the same trend as those of the charge transfer and binding energies discussed earlier.

TABLE 1 The MP2/6–311 + G(d) calculated relative energy (ΔE), binding energy (BE), charge transferred to CO_2 (Δq), spin density located at CO_2 ($\Delta\rho_s$), and SOMO-energy (E_{SOMO}) of superalkali-CO_2 complexes

Systems	Isomer	ΔE (eV)	BE (eV)	Δq (e)	$\Delta\rho_s$ (a.u.)	E_{SOMO} (eV)
FLi_2—CO_2	(a)	0	2.41	−0.90	0.96	−9.74
	(b)	1.07	1.34	−0.17	0.08	−4.35
OLi_3—CO_2	(a)	0	1.23	−0.88	0.96	−8.91
	(b)	0.40	0.83	−0.82	0.89	−8.58
NLi_4—CO_2			1.17	−0.85	0.96	−6.57

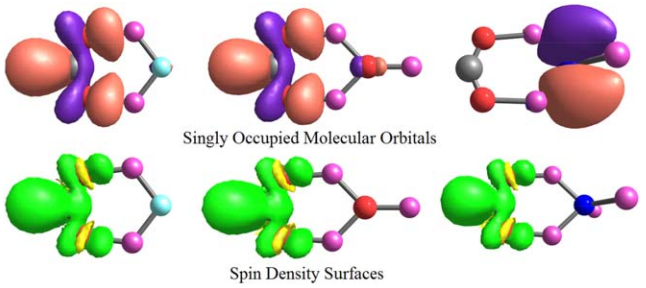

FIGURE 2 The singly occupied molecular orbitals (isovalue = 0.02 a.u.) and spin density surfaces (isovalue = 0.002 a.u.) of superalkali-CO_2 complexes

Thus, superalkalis are indeed capable in the single-electron reduction of CO_2. It should, however, be noticed that the size of superalkalis is more effective than their ionization energy in CO_2 activation. For example, the size of superalkalis considered is in the order, $FLi_2 < OLi_3 < NLi_4$ whereas their ionization energies follow a reverse order, $FLi_2 > OLi_3 > NLi_4$. Our calculated binding energy, charge transfer and SOMO energies of superalkali-CO_2 complexes have suggested that FLi_2 is more effective for CO_2-reduction than NLi_4. Recently, in a combined experimental and theoretical study of $(M{-}CO_2)^-$ anionic complexes (M = Cu, Ag, Au), Zhang et al.[33] noticed that the size of transition metal indeed plays an important role in the charge transfer as CO_2 is found to be bent by 139° for M = Cu but remained almost linear for M = Au. A similar trend has also been observed by Zhao et al.[19] in case of some novel superalkalis.

We have also analyzed the anionic complex of superalkali-CO_2. Note that all superalkali-CO_2 complexes are open shell systems and hence, they are difficult to be introduced in the reaction field. On the contrary, anions of superalkali-CO_2 complexes such as $(FLi_2{-}CO_2)^-$, $(OLi_3{-}CO_2)^-$, $(NLi_4{-}CO_2)^-$ being closed-shell species, can be feasible from the experimental point of view. We obtained three low-lying isomers of $(FLi_2{-}CO_2)^-$ as well as $(OLi_3{-}CO_2)^-$ and two isomers of $(NLi_4{-}CO_2)^-$ anionic complex as displayed in Figure 3. The relative energies (ΔE), binding energy (BE) and charge transfer (Δq) to CO_2 in these isomers are listed in Table 2. The BEs are calculated by considering the excess electron on superalkalis. In all cases, CO_2 assumes a bent structure, except for the higher energy isomer (c) of $(OLi_3{-}CO_2)^-$. The bond angle of CO_2 is significantly reduced in case of $(FLi_2{-}CO_2)^-$, being 122° in (a), 113° in (b), and 111° in (c). This angle remains 137°-130° and 136°-121° in $(OLi_3{-}CO_2)^-$ and $(NLi_4{-}CO_2)^-$, respectively. The BEs of anionic complexes follow the same trend as those of neutral ones, although their values are relatively small (see Table 1). It is evident from Table 2 that the charge transfer (Δq) to CO_2 in the lowest energy structures of $(OLi_3{-}CO_2)^-$ and $(NLi_4{-}CO_2)^-$ is $-0.90e$ and $-0.83e$, respectively, which is close to unity. More interestingly, the Δq of $(FLi_2{-}CO_2)^-$ isomers increases to $-1.57e$ in (a), $-1.90e$ in (b), and $-1.76e$ in isomer (c), becoming very close of $2e$ in magnitude. Thus, CO_2 can be reduced to CO_2^{2-}, when an electron is added to $FLi_2{-}CO_2$ complex. Due to smaller size, FLi_2 superalkali is not only capable to reduce CO_2 more effectively to CO_2^- (single-electron reduction) but also CO_2^- to CO_2^{2-} (double-electron reduction).

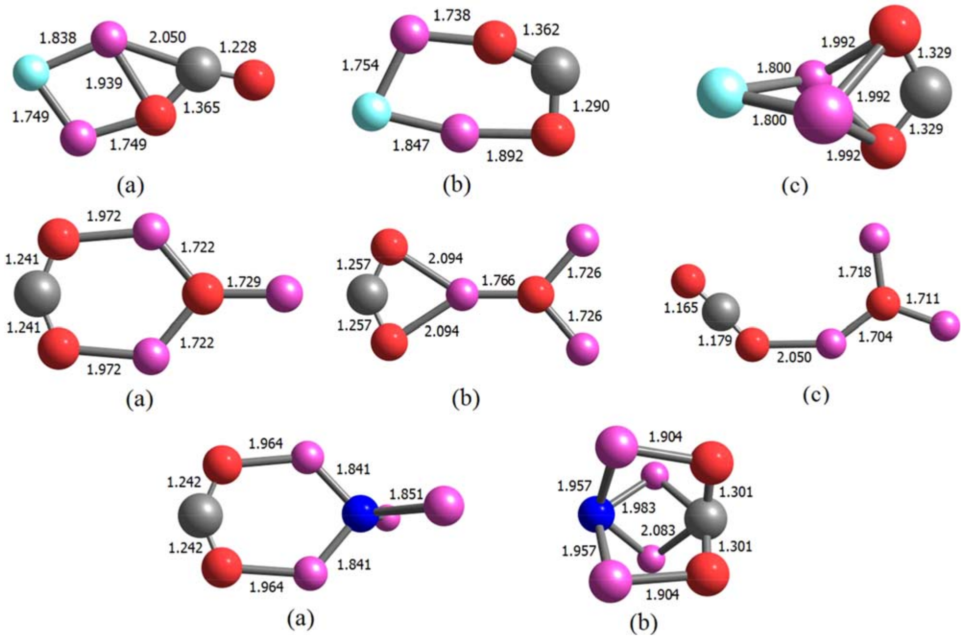

FIGURE 3 Equilibrium structures of superalkali-CO_2 complex anions with bond lengths in Å. Their relative energies are listed in Table 2

TABLE 2 The MP2/6–311 + G(d) calculated relative energy (ΔE), binding energy (BE), and charge transferred to CO_2 (Δq) of superalkali-CO_2 complex anions

Anions	Isomer	ΔE (eV)	BE (eV)	Δq (e)
$(FLi_2\text{—}CO_2)^-$	(a)	0	1.24	−1.57
	(b)	0.01	1.23	−1.92
	(c)	0.07	1.17	−1.73
$(OLi_3\text{—}CO_2)^-$	(a)	0	1.04	−0.90
	(b)	0.31	0.73	−0.82
	(c)	0.83	0.21	−0.01
$(NLi_4\text{—}CO_2)^-$	(a)	0	0.85	−0.83
	(b)	0.71	0.14	−1.48

4 | CONCLUSIONS

Using MP2/6–311 + G(d) calculations, we have studied the interaction of CO_2 by superalkalis such as FLi_2, OLi_3, and NLi_4. We have obtained their lowest energy structures along with possible isomers and calculated various parameters such as binding energy, charge transfer, and spin density. The singly occupied molecular orbitals and spin density surfaces have been also explored. The resulting superalkali-CO_2 complexes are found to be stable in which an electron transfer takes place from superalkali to CO_2 moieties. This unpaired electron is entirely located on the CO_2 moiety, bending it by 133°. Thus, CO_2 can be activated by using superalkalis. Although all superalkalis studied here are capable to reduce CO_2 into CO_2^- anion, the single-electron reduction is more effective in case of smaller superalkali such as FLi_2. It has been also noticed that CO_2^- in the $FLi_2\text{—}CO_2$ complex can be further reduced to CO_2^{2-} by addition of an extra electron. This study should address one of the fundamental problems in the conversion of CO_2 into fuels.

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