

# Superhalogen properties of $\text{CoO}_n$ ( $n \geq 3$ ) species revealed by density functional theory

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**Abstract** A systematic study on  $\text{CoO}_n$  species for  $n = 1-5$  in neutral and (mono)anionic forms has been performed using hybrid exchange-correlation functional in density functional theory. The ground-state structures are obtained, and their stabilities are analyzed against dissociation to O atom and  $\text{O}_2$  molecule. We find that Co can bind stably up to four O atoms, expanding its oxidation state to +8. The adiabatic electron affinities of  $\text{CoO}_n$  and vertical detachment energies of  $\text{CoO}_n^-$  reveal their superhalogen behavior for  $n \geq 3$  due to extra electron delocalization over O atoms.  $\text{CoO}_n$  superhalogens can be used to form a new class of complex compounds. This idea is demonstrated by formation of stable  $\text{LiCoO}_4$  complex by interacting Li atom with  $\text{CoO}_4$  superhalogen.

**Keywords** Cobalt oxides · Superhalogen · Lithium complex · Stability · Electron affinity

## 1 Introduction

Halogen atoms possess the highest electron affinity (EA) among all the elements in the periodic table, but limited to 3.62 eV for Cl [1]. The term ‘superhalogen’ is associated with the molecular species whose electron affinities (EAs) exceed to that of halogen atoms. The concept of superhalogen introduced by Gutsev and Boldyrev [2] and its experimental verification by Wang et al. [3] have provided opportunities to find novel potential oxidizers. Bartlett and

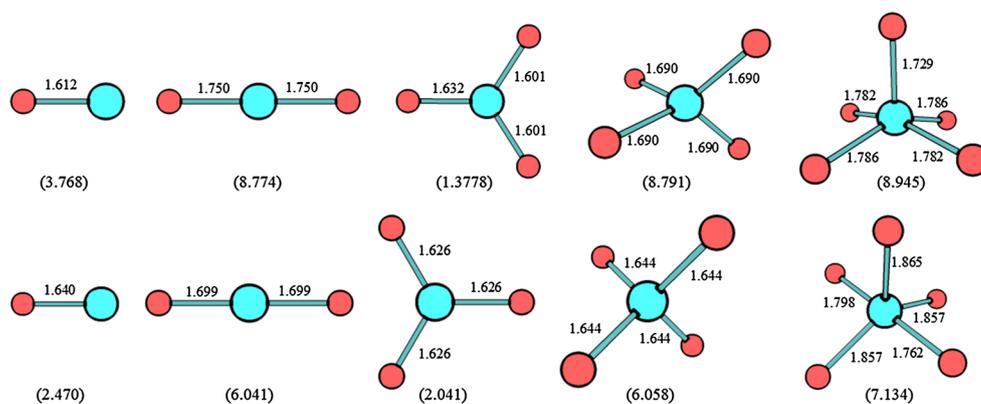
Lohmann have already noticed the capability of  $\text{PtF}_6$  to oxidize both  $\text{O}_2$  molecule and Xe atom having very high ionization potentials of about 12 eV. This is attributed to an enormous EA of  $\text{PtF}_6$  which is 6.8 eV [4, 5]. The concept of superhalogen was initially proposed for sp group elements. For instance, the EAs of  $\text{LiF}_2$ ,  $\text{BeF}_3$ , etc. [6–9], allow them to be classified as superhalogens. The enhanced EAs of such species result due to delocalization of extra electron over electronegative atoms. In subsequent studies, transition metal-based superhalogens have been investigated as they are known to possess variable coordination number due to the presence of d orbital electrons. A number of transition metal fluorides [10–13], chlorides [14–16] and oxides [17–20] have been reported whose EAs are found to be much higher than halogens. For example, manganese (Mn), a 3d transition metal with configuration  $3d^5s^2$  with seven electrons in its outermost orbital, behaves as superhalogen when combined with four oxygen atoms i.e.,  $\text{MnO}_4$  (EA = 5 eV) [21]. Needless to say, its compound  $\text{KMnO}_4$  is a well-known oxidizing agent.

Ferromagnetic metals such as Fe, Co and Ni belong to the 3d transition metal series. Gutsev et al. [22] have estimated the EA of  $\text{FeO}_4$ , 3.8 eV, which is higher than that of Cl. Therefore,  $\text{FeO}_4$  belongs to the class of superhalogens. Recently, we have performed a systematic study on the nickel group transition metal oxides [23]. We have noticed that the EAs of  $\text{NiO}_n$  for  $n \geq 3$  are higher than those of halogen. However, for  $n = 4$ ,  $\text{NiO}_n$  exists in the form of  $(\text{NiO}_2)_2\text{O}_2$  complex rather than in tetra-oxide form. A natural question arises about Co, can it form stable tetra-oxide, i.e.,  $\text{CoO}_4$ ? Note that Co possesses valence configuration of  $3d^74s^2$  and hence its oxidation state ranges from +2 to +5. In present study, we discuss the structures of neutral and anionic  $\text{CoO}_n$  up to  $n = 5$ . Their stabilities are analyzed by considering the dissociations to O atom and  $\text{O}_2$  molecule.

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**Fig. 1** Equilibrium ground-state structures of neutral (*upper set*) and anionic (*lower set*)  $\text{CoO}_n$  species. Blue circles represent Co atoms, and red circles represent O atoms. Bond lengths (in Å) and  $\langle S^2 \rangle$  values (in brackets) are also given



**Table 1** Relative energies (in kJ/mol) for different spin multiplicities ( $2S + 1$ ) of neutral and anionic  $\text{CoO}_n$  species

$n$	$\text{CoO}_n$			$\text{CoO}_n^-$		
	$2S + 1$	2	4	1	3	5
1		67	0	296	0	25
2		66	0	56	71	0
3		0	17	123	0	68
4		20	15	100	16	0
5		14	7	198	2	0

We find that Co can bind stably up to four O atoms, thus forming stable  $\text{CoO}_4$ . The  $\text{CoO}_n$  species behave as superhalogens for  $n \geq 3$ . Furthermore, we have demonstrated that  $\text{CoO}_4$  superhalogen may interact with Li atom to form stable  $\text{LiCoO}_4$  complex.

## 2 Computational details

All neutral and anionic  $\text{CoO}_n$  structures considered in this study were fully optimized without any symmetry constraint in the potential energy surface. For optimization, density functional theory (DFT) in the form of a hybrid exchange-correlation functional, B3LYP [24, 25], has been employed, and all atoms were described using Stuttgart–Dresden–Dunning (SDD) basis and corresponding pseudopotentials. By comparing a number of methods, it has been noticed that B3LYP calculated results are comparable to high-level ab initio CCSD(T) method [26, 27]. In a recent study, we have also noticed the superiority of B3LYP over MP2 method [28]. In order to check the validity of the SDD basis set in the present case, we have performed some test calculations on neutral and anionic CoO using a more complete basis set, aug-cc-pVDZ, which employs polarization as well as diffuse function. The B3LYP/aug-cc-pVDZ scheme provides quartet CoO (1.593 Å) and triplet  $\text{CoO}^-$  (1.627 Å) as their ground states and the electron affinity of CoO as 1.60 eV. These results are in accordance with those obtained with B3LYP/SDD scheme (see Fig. 1; Table 3,

below). The geometry optimization is followed by vibrational frequency calculation in order to ensure that the optimized structures correspond to true minima in the potential energy surfaces. The same calculations are repeated for higher spin multiplicities in order to locate the ground spin state of each  $\text{CoO}_n$  species.

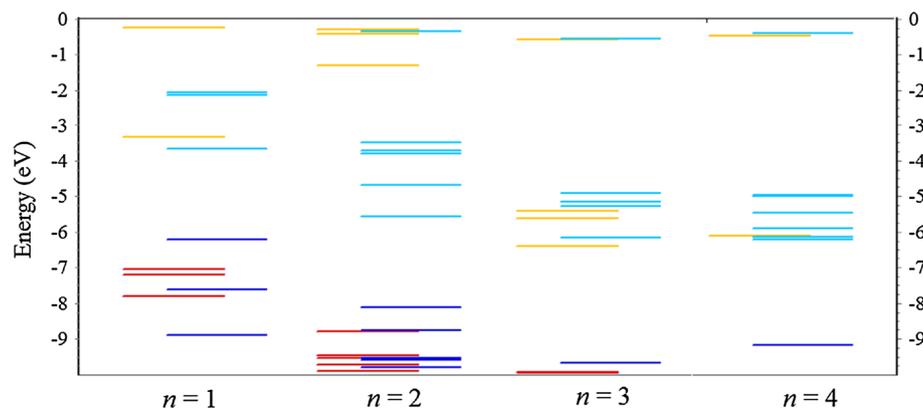
All these calculations are carried out with the help of Gaussian 09 program [29]. The partial charges on Co atom are obtained using natural bonding orbital (NBO) analyses by NBO 3.1 program [30] as implemented in Gaussian 09. The NBO charges are more reliable due to their less dependency on the basis set [31]. Furthermore, in a recent study, we found that the NBO charges perform better than the charges obtained by various other schemes, viz., Mulliken, Hirshfeld and APT [32].

## 3 Results and discussion

The ground-state equilibrium geometries of neutral and anionic  $\text{CoO}_n$  species are displayed in Fig. 1. Table 1 lists the total energies of  $\text{CoO}_n$  species including zero-point correction for different spin multiplicities, viz., doublet, quartet and sextet for neutral, and singlet, triplet and quintet for anion. One can note that except  $\text{CoO}_3$ , all  $\text{CoO}_n$  species tend to favor higher spin multiplicities energetically, irrespective of their charges. From Fig. 1, it is also clear that the structures of  $\text{CoO}_n$  are independent of their charges, i.e., approximately similar in neutral and anions.

**Table 2** Dissociation energies ( $E_{\text{diss}}$ , in eV) and HOMO–LUMO energy gaps ( $E_{\text{gap}}$ , in eV) of neutral and anionic  $\text{CoO}_n$  species

$n$	$\text{CoO}_n$			$\text{CoO}_n^-$		
	$E_{\text{diss}}$		$E_{\text{gap}}$	$E_{\text{diss}}$		$E_{\text{gap}}$
	$\text{CoO}_{n-1} + \text{O}$	$\text{CoO}_{n-2} + \text{O}_2$		$\text{CoO}_{n-1}^- + \text{O}$	$\text{CoO}_{n-2}^- + \text{O}_2$	
1	5.91		2.53			1.76
2	6.41	4.36	2.56	8.04		2.55
3	4.62	3.16	3.28	5.88	6.04	3.79
4	3.89	0.64	2.96	3.68	1.68	2.73
5	2.94	−1.04	2.54	3.40	−0.80	2.62

**Fig. 2** Molecular orbital (MO) diagram of  $\text{CoO}_n$  species ( $n = 1-4$ ). Red and blue lines correspond to the occupied  $\alpha$  (spin up) and  $\beta$  (spin down) orbitals, respectively. Yellow and sky blue correspond to unoccupied  $\alpha$  and  $\beta$  orbitals, respectively

The equilibrium structure of  $\text{CoO}_2$  is approximately linear ( $C_{2v}$ ) unlike perfect linear ( $D_{\infty h}$ ) structure of  $\text{CoO}_2^-$ .  $\text{CoO}_3$  is a trigonal planar in which one of the bond lengths is increased in contrast to equilateral  $\text{CoO}_3^-$ .  $\text{CoO}_4$  and its anion assume tetrahedral structure. Neutral  $\text{CoO}_5$  takes  $C_2$  symmetry, whereas its anion takes  $C_1$ . However, we will show later that  $\text{CoO}_5$  and its anion are thermodynamically unstable as they dissociate into  $\text{CoO}_3 + \text{O}_2$  fragments. In order to check whether the calculated ground states are spin contaminated, we have also listed the expectation value of spin squared ( $\langle S^2 \rangle$ ) in Fig. 1. One can see that almost all the calculated spin states are pure, having  $\langle S^2 \rangle$  values with  $\pm 10\%$  of  $s(s+1)$ , where  $s$  is the total spin of unpaired electrons. However, a significant mixing of spin states can be seen in case of  $\text{CoO}_3$  (doublet) whose  $\langle S^2 \rangle$  value is 1.38 in contrast to the expected value of 0.75. Therefore, it has significant mixing of its higher spin states which is consistent with the small difference in their energy values (see Table 1).

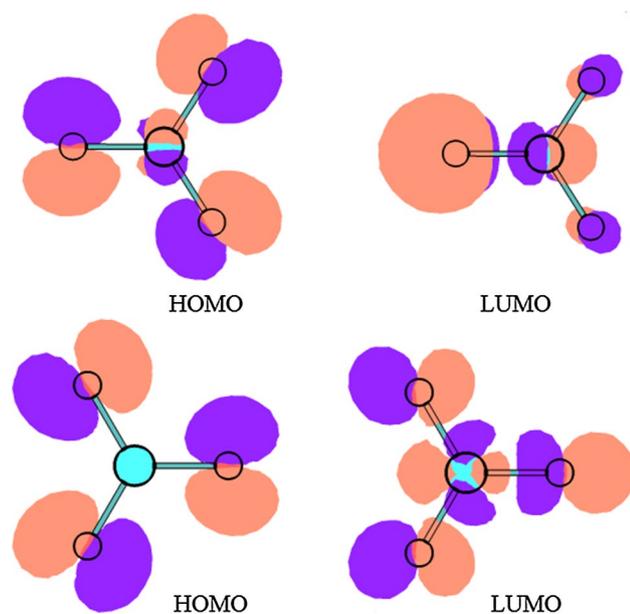
The frequency calculations performed over equilibrium geometries provide all real values which imply that these structures belong to at least some local minima in the potential energy surfaces. In order to further analyze the stability of  $\text{CoO}_n$  species, we consider their dissociations into  $\text{CoO}_{n-1} + \text{O}$  and  $\text{CoO}_{n-2} + \text{O}_2$  fragments. The

corresponding dissociation energies are calculated as below;

$$E_{\text{diss}} = E[\text{O}] + E[\text{CoO}_{n-1}^{o,-}] - E[\text{CoO}_n^{o,-}];$$

$$= E[\text{O}_2] + E[\text{CoO}_{n-2}^{o,-}] - E[\text{CoO}_n^{o,-}]; \quad n = 1-5$$

here  $E[\dots]$  represents the total energy of respective species including zero-point energy correction. The superscripts ‘o’ and ‘-’ correspond to neutral and anions, respectively. The energies of O atom and  $\text{O}_2$  molecule are calculated in their ground spin (triplet) states. The calculated dissociation energies ( $E_{\text{diss}}$ ) for neutral and anionic  $\text{CoO}_n$  species are listed in Table 2. All  $\text{CoO}_n$  species are found to be stable against all possible dissociations, except  $\text{CoO}_5$  and  $\text{CoO}_5^-$  which dissociate into  $\text{CoO}_3 + \text{O}_2$  and  $\text{CoO}_3^- + \text{O}_2$  fragments, respectively. This suggests that  $\text{CoO}_n$  ( $n \leq 4$ ) species can be synthesized by using O atom or  $\text{O}_2$  molecule in their synthesis. In general, the stability of  $\text{CoO}_n$  species decreases with the increase in  $n$  due to the decrease in  $E_{\text{diss}}$  values. It is also interesting to note that  $\text{CoO}_3$  favors dissociation into  $\text{CoO}_2 + \text{O}$  as compared to its anionic counterpart by 1.26 eV. This is in contrast to  $\text{CoO}_4$  whose dissociation requires additional 0.21 eV as compared to its anion. This fact is consistent with higher EA of  $\text{CoO}_3$  than  $\text{CoO}_4$  as discussed below.



**Fig. 3** Molecular orbital (MO) surfaces of  $\text{CoO}_3$  (upper set) and  $\text{CoO}_3^-$  (lower set)

**Table 3** Adiabatic electron affinity (AEA, in eV), vertical detachment energy (VDE, in eV) and NBO charges on Co ( $Q$ , in e)

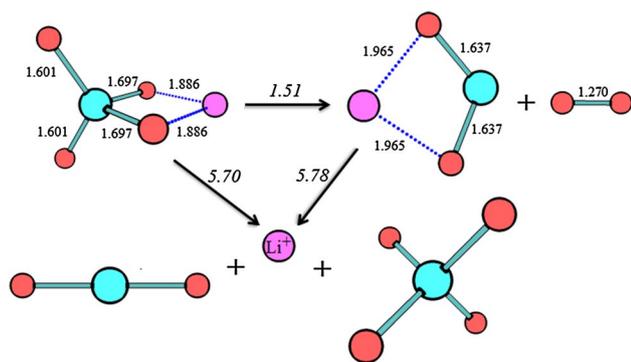
$n$	$\text{CoO}_n$		$\text{CoO}_n^-$	
	$Q$	AEA	$Q$	VDE
1	0.72	1.64	-0.12	2.34
2	1.10	3.26	0.84	4.21
3	0.62	4.52	0.59	4.60
4	0.55	4.31	0.56	4.72
5	0.36	4.76	0.51	4.82

The molecular orbitals (MOs) spectra of neutral  $\text{CoO}_n$  species are displayed in Fig. 2. One can note that both the energies of the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) are negative and, hence, electronically stable. With the increase in  $n$ , the LUMO of  $\text{CoO}_n$  species goes on decreasing. This may indicate the increase in their EAs, as the negative of energy eigenvalues of LUMO approximates the EA of species according to Koopmans' theorem. The energy gap between HOMO and LUMO ( $E_{\text{gap}}$ ) is an important parameter for describing the chemical reactivity of molecular species. The species with smaller  $E_{\text{gap}}$  values are chemically less hard and, therefore, more reactive. On the contrary, the species with larger  $E_{\text{gap}}$  are chemically more stable. The  $E_{\text{gap}}$  values of neutral  $\text{CoO}_n$  lie in the range 2.53–2.96 eV, which are slightly larger than those of  $\text{CoO}_n^-$  anions, 1.76–2.73 eV. However, for  $n = 3$ , the  $E_{\text{gap}}$  of  $\text{CoO}_3^-$  is slightly larger than that of  $\text{CoO}_3$ . This may imply that  $\text{CoO}_3$  is more stabilized

by addition of an extra electron. In order to explain this, we have plotted HOMO and LUMO surfaces of  $\text{CoO}_3$  and its anion in Fig. 3. One can see that the LUMO of  $\text{CoO}_3$  mainly localized on a single O atom and the contribution of the remaining  $\text{CoO}_2$  moiety is only marginal. With the capture of an electron, the HOMO of  $\text{CoO}_3^-$  shows delocalization of electron over O atoms (see Fig. 3). This is consistent with the highest EA of  $\text{CoO}_3$  among all stable  $\text{CoO}_n$  species, as discussed below.

Adiabatic EA (AEA) of  $\text{CoO}_n$  species is calculated by the difference of total energies of neutral and anions including zero-point correction in both their ground-state equilibrium structures. We have also calculated the vertical detachment energy (VDE) of  $\text{CoO}_n^-$  anions. The VDEs are calculated by the difference of total energies of neutral and anions excluding zero-point correction at anion's equilibrium geometry. From Table 3, one can note that the AEA and VDE increase successively with the increase in O atoms. Note that Co has outer orbital configuration of  $3d^7 4s^2$ . In the bonding of  $\text{CoO}$ ,  $4s$  orbital of Co interacts with  $2p$  orbital of O atom, but not  $3d$  orbital. For  $\text{CoO}_2$ , both  $4s$  and  $3d$  electrons of Co participate in bonding with O atoms, leaving exactly half-filled  $3d$  orbital. Note that +2 and +4 are well-established oxidation states of Co. For  $n \geq 3$ , the participation of  $3d$  orbital in bonding of  $\text{CoO}_n$  increases. This causes increasing the coordination number of Co successively with the increase in O atoms. The oxidation state of Co can be as high as +7 due to the enhanced stability of  $\text{CoO}_4^-$  as compared to its neutral counterpart (see Table 2). The AEA of  $\text{CoO}_n$  and VDE of  $\text{CoO}_n^-$  is much higher than the EA of Cl (3.62 eV) [30] for  $n \geq 3$ , allowing  $\text{CoO}_n$  species to behave as superhalogens. The AEA of  $\text{CoO}_4$ , 4.31 eV, is higher than that of  $\text{FeO}_4$ , 3.8 eV [22].

The rise in AEA and VDE of  $\text{CoO}_n$  with the increase in O atoms can be understood in terms of electronic charge distribution. In Table 3, we also list the NBO charges on Co atom in  $\text{CoO}_n$  and  $\text{CoO}_n^-$  species. We can see that the NBO charges on Co increase up to 1.1 e for  $\text{CoO}_2$  and then decrease to 0.55 e for  $\text{CoO}_4$ . Thus, the addition of two more O atoms to  $\text{CoO}_2$  reduces the charge transfer to O atoms by 50%. On the other hand, in  $\text{CoO}^-$ , about 85% of extra electron is contained by Co atom. The extra electron located on Co decreases to 25% in case of  $\text{CoO}_2^-$ , which results in the increase in the AEA of  $\text{CoO}_2$  and VDE of  $\text{CoO}_2^-$ . For  $n \geq 3$ , the extra electron is completely delocalized over O atoms, which leads to very high AEA of  $\text{CoO}_n$  and VDE of its anions. For instance, in  $\text{CoO}_3^-$ , more than 99% of extra electron is contained by peripheral O atoms and merely 0.03% is located on Co. Thus,  $\text{CoO}_3$  and  $\text{CoO}_4$  indeed belong to the class of superhalogens.  $\text{CoO}_n$  superhalogens can be employed to form new class of compounds having unusual oxidizing potentials. Furthermore,  $\text{CoO}_4$



**Fig. 4** Equilibrium structure of  $\text{LiCoO}_4$  complex and its dissociation into stable  $\text{LiCoO}_2$  compound and  $\text{O}_2$  molecule. The bond lengths (in Å) and dissociation energies (in eV, *italicized*) are also shown

can be supposed to be stronger oxidizer as compared to  $\text{FeO}_4$  superhalogen due to its higher EA.

The above discussion suggests that  $\text{CoO}_n$  species behave as superhalogens for  $n \geq 3$ . In order to study the interaction of  $\text{CoO}_4$  superhalogen with Li atom, we put a Li atom on the top of  $\text{CoO}_4$ . After optimization, we find a  $C_s$  structure in which Li binds with two O atoms as shown in Fig. 4. The frequency calculations confirm that this structure belongs to at least some local minimum. In order to discuss the nature of interaction between Li and  $\text{CoO}_4$ , first we analyze the geometry  $\text{CoO}_4$  fragment in  $\text{LiCoO}_4$  complex. The +1 oxidation state of Li leaves  $\text{CoO}_4$  fragment in anionic form. This may suggest the ionic character of the interaction between Li and  $\text{CoO}_4$  superhalogen. Furthermore, the NBO charge on Li atom in  $\text{LiCoO}_4$  complex is found to be 0.88  $e$  which is very close to unity. This may suggest that the interaction of Li atom with  $\text{CoO}_4$  superhalogen is similar to that between Li and halogen atom, i.e., ionic.

The binding energy of  $\text{LiCoO}_4$  against dissociation to Li and  $\text{CoO}_4$  is 4.39 eV, and  $E_{\text{gap}}$  value (2.12 eV) is slightly smaller than that of  $\text{CoO}_4$ . Thus, it may be possible to realize a stable  $\text{LiCoO}_4$  compound by interaction of  $\text{CoO}_4$  superhalogen with Li atom. To examine whether the formation of  $\text{LiCoO}_4$  is energetically favorable, we consider the dissociation of  $\text{LiCoO}_4$  into two stable species, viz.,  $\text{LiCoO}_2$  compound and  $\text{O}_2$  molecule also shown schematically in Fig. 4. The energy required to fragment  $\text{LiCoO}_4$  into  $\text{LiCoO}_2 + \text{O}_2$  is 1.51 eV which advocates the possibility to synthesize  $\text{LiCoO}_4$  compound. Note that  $\text{LiCoO}_2$  finds application as a cathode material in lithium ion batteries. It contributes a lithium ion by dissociating into ionic fragments. To analyze this, we have considered the fragmentation of  $\text{LiCoO}_2$  into  $\text{Li}^+$  and  $\text{CoO}_2^-$  which requires an energy amount of 5.78 eV (see Fig. 3). Similarly, the dissociation of  $\text{LiCoO}_4$  complex into  $\text{Li}^+$  and  $\text{CoO}_4^-$  fragments takes place with the energy value of 5.70 eV which is very close to that of  $\text{LiCoO}_2$ . This may suggest the possibility

of  $\text{LiCoO}_4$  complex as new cathode material in lithium ion batteries.

## 4 Conclusions

Using density functional theory at B3LYP level, we have discussed the structural properties of the ground-state  $\text{CoO}_n$  species up to  $n = 5$  in their neutral and anionic forms. Their stabilities are analyzed by considering dissociations to O atom and  $\text{O}_2$  molecule. All  $\text{CoO}_n$  species are found to be stable for  $n \leq 4$ , suggesting the highest possible oxidation state of Co as +8. The electron affinities of  $\text{CoO}_n$  and vertical detachment energies of  $\text{CoO}_n^-$  are calculated and explained on the basis of extra electron delocalization over O atoms. The superhalogen behavior of  $\text{CoO}_n$  has been established due to their larger electron affinities as compared to halogen for  $n \geq 3$ . The possibility of formation of a new complex compound  $\text{LiCoO}_4$  has also been explored considering the interaction of  $\text{CoO}_4$  superhalogen with Li atom.

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## Compliance with Ethical Standards

**Conflict of interest** The manuscript has been prepared as per ethical guidelines. The authors declare no conflict of interests in the publication of this work.

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