

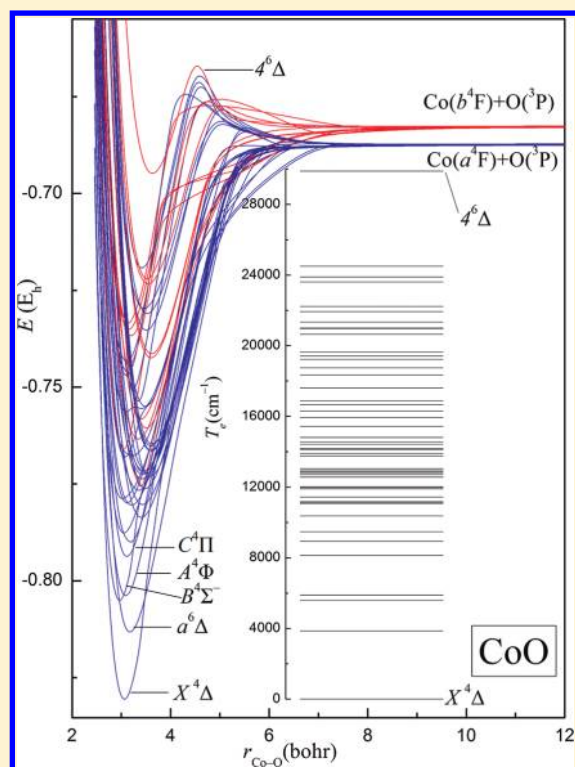
Electronic Structure and Bonding of Cobalt Monoxide, CoO, and Its Ions CoO^+ and CoO^- : An Ab Initio Study

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Supporting Information

ABSTRACT: We present a systematic and high-level ab initio study of CoO and its ions, CoO^+ and CoO^- . Employing variational multi-reference (MRCI) and single-reference coupled-cluster methods combined with basis sets of quintuple quality, we have calculated 50, 31, and 7 bound states for CoO, CoO^+ , and CoO^- , respectively. For all these states, complete potential energy curves have been constructed at the MRCI level of theory, whereas for a few low-lying states core subvalence and scalar relativistic effects have been taken into account. We report energetics, spectroscopic parameters, dipole moments, and spin-orbit coupling constants. The ground states of CoO, CoO^+ , and CoO^- are $X^4\Delta$, $X^5\Delta$, and $X^5\Delta$, respectively, the latter established for the first time. The CoO is quite ionic with a Co to O Mulliken charge transfer of ~ 0.6 electrons and a dipole moment $\mu(X^4\Delta) = 4.5 \pm 0.1$ D. The overall agreement between theory and experiment is good, but there are also important deviations. Despite the seeming simplicity of these diatomic species, reliable results can only be obtained at a high level of theory.



I. INTRODUCTION

The present study of cobalt monoxide and its ions (CoO , CoO^\pm) is related to our previous work on the 3d transition metal oxides $\text{MO}^{0,\pm}$, $M = \text{Sc, Ti, V, Cr, Mn, and Fe}$ (refs 1–3). Despite their chemical simplicity, 3d MO diatomics are very demanding systems both computationally and experimentally,⁴ not yielding easily even to high-level methods of solving the eigenvalue Schrödinger equation. The causes for the great difficulties of obtaining reliable theoretical results on the 3d MO series are well-known and there is no need to discuss it here;^{1–3} see also refs 5 and 6.

Experimental work on CoO extends to 16 publications;^{7–22} see also the review article by Merer.⁴ As early as 1945, Rosen⁷ reported an harmonic frequency for the ground state of CoO, $\omega_e = 840 \text{ cm}^{-1}$. A first estimation of the binding energy was given in 1966 by Grimley et al.,⁸ $D_0^0 = 86.4 \pm 3 \text{ kcal/mol}$. Twenty years later, Adam et al.¹¹ established through laser-induced fluorescence spectroscopy that the ground state of CoO is of $^4\Delta$ symmetry; until then it was believed to be $^4\Sigma^-$.^{9,10} In 1993 Ram et al.¹⁴ using

FTIR emission spectroscopy reported along with the ground state a $^4\Pi$ state with $r_e = 1.653 19 (18) \text{ \AA}$, lying $\sim 5500 \text{ cm}^{-1}$ above the $X^4\Delta$. These numbers have been confirmed later on by Danset and Manceron.¹⁹ More recently, Barnes and co-workers¹⁶ recorded through laser excitation beam spectroscopy nearly 100 bands of gaseous CoO in the wavelength region of 430–720 nm. Among their numerous findings, the possibility of a $^4\Sigma^-$ state was suggested lying 3038 cm^{-1} above the ground state. A similar suggestion for the existence of a $^4\Sigma^-$ state at $T \sim 3400 \text{ cm}^{-1}$ was made by Danset and Manceron.¹⁹ Concerning the $X^4\Delta$ state, the most reliable experimental data read as follows: $r_e = 1.628 626 (32) \text{ \AA}^{14}$ or $1.627 862 (1) \text{ \AA}$,²¹ $\omega_e = 862.4 \text{ cm}^{-1}$,¹⁶ $D_0^0 = 4.08 \pm 0.09 \text{ eV}$ ($=94.1 \pm 2.1 \text{ kcal/mol}$),²⁰ and EA (electron affinity) = $1.45 \pm 0.01 \text{ eV}$.^{11,17}

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The theoretical literature on CoO consists of three ab initio^{23–25} and 10 density functional theory (DFT)²⁶ publications. The DFT results, as usual, at least for this type of molecules, depend upon the functional used. In 1987, Dolg et al.²³ calculated through CISD and adjusted ab initio relativistic pseudopotentials the $^4\Delta$ and $^4\Sigma^-$ states, suggesting the $^4\Delta$ as the ground state. Later on, Bauschlicher and Maitre²⁴ studied the ground states of the isovalent MO and MS series ($M = \text{Sc–Cu}$) by multireference averaged coupled pair functional (MR-ACPF) and coupled-cluster CCSD(T)/[7s6p4d3f2g/maug-cc-pVQZ/o,s] methods. For the $X^4\Delta$ of CoO, they found $r_e = 1.621 \text{ \AA}$, $D_0^0 = 83.9 \text{ kcal/mol}$, $\omega_e = 909 \text{ cm}^{-1}$, and $\mu = 3.46 \text{ D}$. Very recently, Baranowska et al.²⁵ obtained $\mu = 5.13$ (CASPT2) and 4.71 D (CCSD(T)) using single-point ($r_e = 1.621 \text{ \AA}$) calculations, combined with reduced-size polarized basis sets; corresponding values including scalar relativistic effects are $\mu = 5.42$ and 4.64 D , respectively. There is no experimental value of the dipole moment of CoO.

We move now to the cation, CoO^+ . From the Armentrout group we do know the binding energy of CoO^+ , $D_0^0 = 75.9 \pm 1.4^{12}$ or $76.1 \pm 1.6 \text{ kcal/mol}$,¹³ and the ionization energy of CoO, $\text{IE} = 8.69 \pm 0.20 \text{ eV}$.¹² Through rotational photodissociation spectroscopy the ground-state symmetry of CoO^+ was recently determined to be $^5\Delta_4$ with $r_0 = 1.65 \pm 0.01 \text{ \AA}$ by Kamariotis et al.²⁷ In addition, these workers determined two more states, $B^5\Phi_3$ and $C^5\Pi_3$, with $T_0 = 16\,713 \pm 10$ and $17\,588 \pm 10 \text{ cm}^{-1}$ at $r_0 = 1.87 \pm 0.01$ and $1.86 \pm 0.015 \text{ \AA}$, respectively.

The first theoretical work on CoO^+ was published in 1988 by Carter and Goddard.²⁸ Ten years later, Sodupe and co-authors²⁹ reported CCSD(T) and DFT/B3LYP calculations on the ground states of the MO^+ series, $M = \text{Sc–Cu}$. The most recent theoretical work on CoO^+ is that of Nakao et al.³⁰ These workers examined 16 states of CoO^+ around equilibrium by multi-reference configuration interaction methods, using the Stuttgart relativistic small core effective potential for the $1s^2 2s^2 2p^6$ electrons of Co and a [6s5p3d1f/c_oaug-cc-pVTZ/o] basis set; they report r_e , D_0 , and ω_e . Their results will be contrasted with ours later on. Finally, among other molecular species, two more DFT works on CoO^+ have appeared in the literature.^{26e,31}

For the anion, CoO^- , the only experimental parameter known is its ionization energy, $\text{IE} = 1.45 \pm 0.01 \text{ eV}$.^{11,17} Theoretical work is limited to DFT calculations,^{26b,d,f,i} predicting either a $^5\Delta$ (DFT/B1LYP)^{26d,i} or a $^3\Sigma^-$ (DFT/B3LYP)^{26f} ground state. The ground state of CoO^- has yet to be determined experimentally. Our results clearly indicate a $^5\Delta$ ground state followed by two low-lying states of $^3\Phi$ and $^3\Sigma^-$ symmetries (vide infra).

This literature survey shows the need for systematic high-level ab initio calculations on the $\text{CoO}^{0,\pm}$ species. To that end, we have performed variational multireference configuration interaction and single-reference coupled-cluster calculations, combined with extended correlation consistent basis sets. We have constructed full potential energy curves (PEC) for 50, 31, and 7 bound states of CoO, CoO^+ , and CoO^- , respectively, reporting common spectroscopic parameters, dissociation energies, dipole moments, separation energies, and spin-orbit coupling constants.

This paper is structured as follows. In section II we give some technical details; sections IIIA, IIIB, and IIIC refer to results and discussion on CoO, CoO^+ , and CoO^- , respectively; and a final section IV epitomizes our findings.

II. TECHNICAL ASPECTS

The correlation consistent basis set of quintuple cardinality by Balabanov and Peterson³² was used for the Co atom combined

with the corresponding augmented basis set for the O atom, aug-cc-pV5Z.^{33,34} Both sets were generally contracted to [9s8p6d4f3g2h1i/c_o7s6p5d4f3g2h/o] $\equiv \text{A5}\zeta$. This Gaussian set of order 280 was used for the construction of all potential energy curves (PEC). To account for the $3s^2 3p^6$ subvalence core electrons of the Co atom, the weighted core cc-pwCV5Z set was employed in the CI calculations.³² This means that the A5 ζ basis set was enriched by a set of weighted core functions, (2s2p2d1f1g1h1i), and then generally contracted to [11s10p8d5f4g3h2i/c_o7s6p5d4f3g2h/o] ($\equiv \text{CA5}\zeta$) of order 338.

All PECs have been calculated by the complete active space self-consistent field (CASSCF) + single + double replacements (CASSCF + 1 + 2 = MRCI) method under C_{2v} symmetry restrictions. The CASSCF reference wave functions are defined by allotting 13 (CoO), 12 (CoO^+), and 14 (CoO^-) electrons to nine “valence” orbitals ($4s + 3d/c_o + 2p/o$). Internally contracted (ic)³⁶ valence MRCI wave functions were calculated by single + double excitations out of the reference spaces including the 2s electrons of the O atom. For a limited number of low-lying states, the single-reference (based on CASSCF natural orbitals) restricted coupled-cluster + iterative singles + doubles + quasiperturbative connected triples approach, RCCSD(T),³⁵ was also employed. Correlation effects of the subvalence electrons of the Co atom ($3s^2 3p^6$) were taken into account by including them in the MRCI and RCCSD(T) calculations, named C-MRCI and C-RCCSD(T). For the first 5 states of CoO and CoO^+ and the 7 states of CoO^- , the inclusion of the 4p (Co) and 2s (O) orbitals in the reference space resulted in much larger expansions, tagged MRCI-L. These calculations were only possible by limiting the excitations to the 4p space to singles and doubles. The size of the icMRCI (MRCI), icC-MRCI (C-MRCI), and icMRCI-L (MRCI-L) expansions for the $X^4\Delta$ ground state of CoO, for instance, are 1.5×10^6 (2.2×10^8), 6.8×10^6 (1.3×10^9), and 6.7×10^7 (7.9×10^9) configuration functions. Of course, all our MRCI calculations are of the internally contracted type.

Scalar relativistic effects for a few low-lying states were estimated by the second-order Douglas–Kroll–Hess (DKH2) approach.^{37,38} For the DKH2 calculations, the A5 ζ and CA5 ζ basis sets were recontracted accordingly.³² Spin-orbit (SO) couplings constants (A) are obtained by diagonalizing the $\hat{H}_e + \hat{H}_{SO}$ Hamiltonian within the \hat{H}_e MRCI/A5 ζ eigenvectors, where \hat{H}_{SO} is the full Breit–Pauli operator. Basis set superposition errors (BSSE) estimated by the usual counterpoise method,³⁹ are about 0.4 kcal/mol or less. Spectroscopic parameters have been determined by solving numerically the one-dimensional Schrödinger equation. The size nonextensivity error (SNE) estimated by subtracting the sum of the energies of the atoms from the total energy of the supermolecule at the internuclear distance of 30 bohr is, for instance, $\text{SNE}(X^4\Delta) = 19$ (7) and 33 (11) mE_h at the MRCI (+Q)/A5 ζ and C-MRCI(+Q)/CA5 ζ level, respectively, where +Q refers to the Davidson correction.⁴⁰ To further reduce the SNE we have performed multireference averaged coupled-pair functional (ACPF)⁴¹ calculations for a few states of CoO and the ground states of CoO^{\pm} . At this level for the $X^4\Delta$ state, $\text{SNE} = 0.3$ (ACPF/A5 ζ) and 0.6 mE_h (ACPF/CA5 ζ).

All calculations have been carried out by the MOLPRO2006 suite of codes.⁴²

III. RESULTS AND DISCUSSION

A. CoO. The ground state of the Co atom is $a^4F(4s^2 3d^7)$ with the first two excited states, $b^4F(4s^1 3d^8)$ and $a^2F(4s^1 3d^8)$, 0.4172 and 0.8785 eV higher, respectively.⁴³ The interaction of Co (a^4F) and O(3P), albeit repulsive due to the $4s^2$ distribution of the Co

Table 1. Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal mol⁻¹), Harmonic Frequencies, and Anharmonicity Corrections ω_e , $\omega_e x_e$ (cm⁻¹), Rotational–Vibrational Coupling Constants $\alpha_e \times 10^3$ (cm⁻¹), Dipole Moments μ (D), Mulliken Charges on Co q_{Co} , and Energy Separations T_e (cm⁻¹) of the First Five States of Co¹⁶O; Experimental Results Are Also Included

| method ^a | $-E$ | r_e | D_e^b | ω_e | $\omega_e x_e$ | α_e | $\langle\mu\rangle/\mu_{FF}^c$ | q_{Co} | T_e |
|--|------------|---------------------|-------------------------|--------------------|-------------------|---------------------|--------------------------------|----------|------------|
| X⁴Δ (a⁴F) | | | | | | | | | |
| MRCI | 1456.78176 | 1.628 | 79.6 | 881 | 5.7 | 3.9 | 3.61/4.50 | 0.54 | 0.0 |
| MRCI+Q | 1456.83115 | 1.619 | 86.0 | 904 | 4.5 | 3.7 | /4.62 | | 0.0 |
| MRCI+DKH2 | 1467.27752 | 1.616 | 78.8 | 894 | 5.1 | 3.9 | 3.63/4.37 | | 0.0 |
| MRCI+DKH2+Q | 1467.32771 | 1.607 | 85.4 | 923 | 5.7 | 3.9 | /4.42 | | 0.0 |
| C-MRCI | 1457.18841 | 1.629 | 76.3 | 879 | 5.3 | 3.9 | 3.61/4.47 | | 0.0 |
| C-MRCI+Q | 1457.28208 | 1.618 | 85.1 | 909 | 4.5 | 3.7 | /4.64 | | 0.0 |
| C-MRCI+DKH2 | 1467.68473 | 1.618 | 75.5 | 893 | 5.6 | 4.0 | 3.64/4.35 | | 0.0 |
| C-MRCI+DKH2+Q | 1467.77935 | 1.606 | 84.4 | 929 | 5.9 | 3.9 | /4.43 | | 0.0 |
| ACPF | 1456.83434 | 1.618 | 86.0 | 909 | 5.1 | 3.7 | 3.41/4.64 | | 0.0 |
| ACPF+DKH2 | 1467.33112 | 1.606 | 85.6 | 924 | 4.4 | 3.8 | 3.40/4.39 | | 0.0 |
| C-ACPF | 1457.29704 | 1.614 | 85.3 | 919 | 4.7 | 3.7 | 3.29/4.61 | | 0.0 |
| C-ACPF+DKH2 | 1467.79481 | 1.603 | 84.8 | 937 | 4.9 | 3.9 | 3.28/4.38 | | 0.0 |
| RCCSD(T) | 1456.85236 | 1.623 | 89.8 | 906 | 4.0 | 3.3 | /4.79 | | 0.0 |
| RCCSD(T)+DKH2 | 1467.34836 | 1.609 | 88.7 | 924 | 3.8 | 3.4 | /4.60 | | 0.0 |
| C-RCCSD(T) | 1457.32910 | 1.625 | 90.3 | 907 | 3.9 | 3.3 | /4.74 | | 0.0 |
| C-RCCSD(T)+DKH2 | 1467.82569 | 1.611 | 88.9 | 926 | 3.6 | 3.3 | /4.55 | | 0.0 |
| MRCI-L | 1456.80560 | 1.626 | 84.8 | 929 | 6.1 | 3.5 | 4.73/4.69 | 0.58 | 0.0 |
| MRCI-L+Q | 1456.84082 | 1.621 | 88.2 | 953 | 6.3 | 3.2 | /4.35 | | 0.0 |
| MRCI-L+DKH2 | 1467.30106 | 1.614 | 83.8 | 938 | 5.9 | 3.5 | 4.60/4.53 | | 0.0 |
| MRCI-L+DKH2+Q | 1467.33665 | 1.609 | 87.1 | 962 | 5.8 | 3.3 | /4.29 | | 0.0 |
| expt | | 1.6279 ^d | 94.1 ± 2.1 ^e | 862.4 ^f | 5.13 ^f | 3.9883 ^d | | | |
| a⁶Δ (a⁴F) | | | | | | | | | |
| MRCI | 1456.77014 | 1.689 | 72.3 | 729 | 4.8 | 4.5 | 1.78/1.87 | 0.58 | 2550 |
| MRCI+Q | 1456.81357 | 1.679 | 75.0 | 748 | 5.3 | 4.7 | /1.75 | | 3857 |
| MRCI+DKH2 | 1467.26421 | 1.682 | 70.4 | 735 | 4.9 | 4.6 | 1.84/1.94 | | 2921 |
| MRCI+DKH2+Q | 1467.30826 | 1.670 | 73.2 | 756 | 5.5 | 4.8 | /1.83 | | 4267 |
| C-MRCI | 1457.17876 | 1.693 | 70.3 | 725 | 4.6 | 4.4 | 1.88/1.92 | | 2117 |
| C-MRCI+Q | 1457.26580 | 1.681 | 74.9 | 748 | 5.1 | 4.6 | /1.82 | | 3572 |
| C-MRCI+DKH2 | 1467.67339 | 1.686 | 68.4 | 730 | 4.7 | 4.5 | 1.93/1.99 | | 2489 |
| C-MRCI+DKH2+Q | 1467.76112 | 1.673 | 73.0 | 753 | 5.3 | 4.7 | /1.89 | | 4000 |
| ACPF | 1456.81496 | 1.677 | 73.9 | 749 | 5.5 | 4.8 | 1.59/1.69 | | 4253 |
| ACPF+DKH2 | 1467.30981 | 1.668 | 72.2 | 758 | 5.7 | 4.9 | 1.62/1.76 | | 4677 |
| C-ACPF | 1457.27690 | 1.677 | 72.6 | 751 | 5.5 | 4.8 | 1.65/1.69 | | 4421 |
| C-ACPF+DKH2 | 1467.77258 | 1.669 | 70.8 | 758 | 5.6 | 4.9 | 1.67/1.77 | | 4879 |
| RCCSD(T) | 1456.82730 | 1.649 | 74.1 | 806 | 7.1 | 5.4 | /1.58 | | 5499 |
| RCCSD(T)+DKH2 | 1467.32305 | 1.643 | 72.9 | 822 | 7.3 | 5.4 | /1.70 | | 5556 |
| C-RCCSD(T) | 1457.30171 | 1.646 | 73.1 | 830 | 7.0 | 5.2 | /1.55 | | 6011 |
| C-RCCSD(T)+DKH2 | 1467.79832 | 1.640 | 71.8 | 842 | 7.0 | 5.2 | /1.66 | | 6006 |
| MRCI-L | 1456.79155 | 1.686 | 76.0 | 734 | 5.0 | 4.6 | 1.69/1.78 | 0.52 | 3082 |
| MRCI-L+Q | 1456.82284 | 1.677 | 76.9 | 757 | 5.4 | 4.7 | /1.72 | | 3947 |
| MRCI-L+DKH2 | 1467.28618 | 1.676 | 74.5 | 747 | 5.4 | 4.8 | 1.77/1.80 | | 3265 |
| MRCI-L+DKH2+Q | 1467.31795 | 1.667 | 75.4 | 771 | 5.9 | 4.8 | /1.78 | | 4104 |
| expt ^g | | 1.686 | | 729.7 | | | | | 7028 ± 1.3 |
| B⁴Σ⁻ (a⁴F) | | | | | | | | | |
| MRCI | 1456.75491 | 1.583 | 62.7 | 904 | 3.1 | 5.9 | 3.50/4.70 | 0.61 | 5894 |
| MRCI+Q | 1456.80568 | 1.568 | 70.0 | 972 | 3.2 | 4.8 | /5.01 | | 5590 |
| MRCI+DKH2 | 1467.24788 | 1.580 | 60.2 | 890 | 3.3 | 6.6 | 3.58/4.53 | | 6506 |
| MRCI+DKH2+Q | 1467.29924 | 1.565 | 67.5 | 965 | 3.2 | 5.2 | /4.80 | | 6247 |
| C-MRCI | 1457.16261 | 1.583 | 60.1 | 898 | 3.4 | 6.4 | 3.51/4.52 | | 5663 |
| C-MRCI+Q | 1457.25740 | 1.565 | 69.6 | 987 | 3.6 | 4.9 | /4.88 | | 5416 |
| C-MRCI+DKH2 | 1467.65621 | 1.581 | 57.6 | 884 | 3.5 | 7.0 | 3.60/4.41 | | 6260 |
| C-MRCI+DKH2+Q | 1467.75160 | 1.562 | 67.0 | 979 | 3.4 | 5.2 | /4.69 | | 6091 |
| RCCSD(T) | 1456.83587 | 1.579 | 79.5 | 961 | 3.6 | 3.2 | /5.60 | | 3618 |
| RCCSD(T)+DKH2 | 1467.32807 | 1.572 | 76.0 | 967 | 3.2 | 3.2 | /5.34 | | 4453 |
| C-RCCSD(T) | 1457.31316 | 1.577 | 80.3 | 961 | 3.0 | 3.2 | /5.58 | | 3498 |
| C-RCCSD(T)+DKH2 | 1467.80612 | 1.569 | 76.6 | 972 | 3.9 | 3.4 | /5.31 | | 4295 |
| MRCI-L | 1456.78371 | 1.594 | 71.1 | 920 | 3.7 | 5.3 | 5.12/5.53 | 0.58 | 4803 |

Table 1. continued

| method ^a | $-E$ | r_e | D_e^b | ω_e | $\omega_e x_e$ | α_e | $\langle \mu \rangle / \mu_{\text{FF}}^c$ | q_{Co} | T_e |
|--|------------|--------|---------|------------|----------------|------------|---|-----------------|------------|
| B⁴Σ⁻ (a⁴F) | | | | | | | | | |
| MRCI-L+Q | 1456.82040 | 1.581 | 75.4 | 978 | 3.6 | 4.4 | /5.47 | | 4481 |
| MRCI-L+DKH2 | 1467.27565 | 1.591 | 67.8 | 891 | 3.5 | 5.9 | 5.07/5.48 | | 5575 |
| MRCI-L+DKH2+Q | 1467.31248 | 1.578 | 71.9 | 952 | 3.4 | 5.1 | /5.12 | | 5306 |
| expt ^g | | 1.641 | | | | | | | 3390 ± 1.3 |
| A⁴Φ (a⁴F) | | | | | | | | | |
| MRCI | 1456.75815 | 1.643 | 64.8 | 792 | 7.2 | 5.0 | 3.47/4.69 | 0.67 | 5182 |
| MRCI+Q | 1456.80430 | 1.633 | 69.2 | 823 | 7.7 | 5.0 | /5.00 | | 5892 |
| MRCI+DKH2 | 1467.25166 | 1.639 | 62.6 | 793 | 7.7 | 5.2 | 3.57/4.69 | | 5674 |
| MRCI+DKH2+Q | 1467.29842 | 1.628 | 67.0 | 825 | 7.2 | 4.9 | /4.96 | | 6428 |
| C-MRCI | 1457.16623 | 1.644 | 62.4 | 785 | 7.1 | 5.1 | 3.44/4.55 | | 4867 |
| C-MRCI+Q | 1457.25603 | 1.632 | 68.8 | 822 | 7.6 | 5.0 | /4.89 | | 5718 |
| C-MRCI+DKH2 | 1467.66040 | 1.640 | 60.2 | 785 | 6.9 | 5.2 | 3.55/4.57 | | 5339 |
| C-MRCI+DKH2+Q | 1467.75088 | 1.627 | 66.5 | 825 | 8.4 | 5.2 | /4.88 | | 6249 |
| MRCI-L | 1456.78763 | 1.639 | 73.5 | 856 | 7.5 | 4.3 | 4.74/6.02 | 0.66 | 3943 |
| MRCI-L+Q | 1456.82031 | 1.633 | 75.3 | 887 | 8.4 | 4.1 | /6.20 | | 4501 |
| MRCI-L+DKH2 | 1467.28080 | 1.634 | 71.1 | 850 | 7.7 | 4.5 | 4.79/5.67 | | 4447 |
| MRCI-L+DKH2+Q | 1467.31380 | 1.628 | 72.7 | 879 | 7.7 | 4.2 | /5.78 | | 5016 |
| C⁴Π (a⁴F) | | | | | | | | | |
| MRCI | 1456.74700 | 1.660 | 57.8 | 741 | 5.9 | 5.3 | 3.55/4.78 | 0.67 | 7630 |
| MRCI+Q | 1456.79411 | 1.644 | 62.8 | 788 | 7.0 | 5.1 | /5.00 | | 8129 |
| MRCI+DKH2 | 1467.24117 | 1.656 | 56.0 | 749 | 5.5 | 5.0 | 3.65/4.79 | | 7978 |
| MRCI+DKH2+Q | 1467.28893 | 1.640 | 61.1 | 791 | 6.4 | 5.0 | /4.98 | | 8511 |
| C-MRCI | 1457.15486 | 1.661 | 55.3 | 731 | 6.2 | 5.5 | 3.52/4.66 | | 7362 |
| C-MRCI+Q | 1457.24562 | 1.642 | 62.2 | 785 | 8.1 | 5.6 | /4.91 | | 8001 |
| C-MRCI+DKH2 | 1467.64966 | 1.658 | 53.5 | 738 | 5.3 | 5.1 | 3.63/4.68 | | 7698 |
| C-MRCI+DKH2+Q | 1467.74114 | 1.639 | 60.4 | 788 | 7.2 | 5.4 | /4.92 | | 8387 |
| MRCI-L | 1456.77600 | 1.652 | 66.2 | 811 | 7.0 | 4.6 | 4.77/6.46 | 0.66 | 6497 |
| MRCI-L+Q | 1456.80917 | 1.641 | 68.3 | 845 | 7.7 | 4.5 | /6.08 | | 6947 |
| MRCI-L+DKH2 | 1467.26995 | 1.648 | 64.3 | 812 | 6.6 | 4.5 | 4.80/5.69 | | 6826 |
| MRCI-L+DKH2+Q | 1467.30337 | 1.638 | 66.2 | 839 | 7.0 | 4.5 | /5.57 | | 7304 |
| expt ^g | | 1.6532 | | | | | | | 5837 ± 1.3 |

^a+Q, DKH2, and C- refer to the Davidson correction for unlinked clusters, Douglas–Kroll–Hess approximation of second order for scalar relativity, and that the subvalence core electrons of Co(3s²3p⁶) have been included in the CI calculations, respectively. Calculations marked by “-L” (MRCI-L, MRCI-L+Q, MRCI+DKH-L, MRCI-L+DKH+Q) have been performed with a larger reference space; see text. ^bWith respect to the ground state atoms, Co(a⁴F) + O(³P). ^cDipole moment calculated as the expectation value $\langle \mu \rangle$, or through the finite-field approach, μ_{FF} ; field strength 10⁻⁵ au. ^dReference 21. ^eReference 20; D_0 value. ^fReference 16. ^gReference 19; see text.

the radius of which is at least 3 times larger than the 3d radius,⁴⁴ gives rise to 36 ^{2S+1}Λ molecular states, namely, ^{2,4,6}(Σ⁺[2], Σ⁻, Π[3], Δ[3], Φ[2], Γ) doublets, quartets, and sextets. Of course, an equal number of states (of the same space–spin symmetry) emanates from the second energy channel, Co(b⁴F) + O(³P). We have studied all 36 states correlating adiabatically to Co(a⁴F) + O(³P), plus 14 more related to the second channel, Co(b⁴F) + O(³P). However, our results indicate (vide infra) that, (a) the CoO system in all states studied is quite ionic with an equilibrium Mulliken charge on Co of about +0.6, and (b) the corresponding occupations of the Co atom are very close to a 4s¹3d⁷ distribution, pointing to an in situ Co⁺ electron configuration. The first two excited states of Co⁺ are a⁵F(4s¹3d⁷) and b³F(4s¹3d⁷), 0.4287 and 1.2118 eV above its ground a³F(d⁸) state, respectively;⁴³ the latter is not involved in the Co + O bonding process. These two Co⁺ terms, a⁵F and b³F, when combined with the ²P term of the oxygen anion give rise to doublets and quartets, and quartets and sextets, that is, ^{2,4}(Σ⁺, Σ⁻[2], Π[3], Δ[3], Φ[2], Γ) and ^{4,6}(Σ⁺, Σ⁻[2], Π[3], Δ[3], Φ[2], Γ), respectively, a total of 24 + 24 = 48 ^{2S+1}Λ molecular states. Therefore, we are inclined in the following discussion to adopt the ionic model Co⁺O⁻ as more pragmatic. Indeed, the construction of 50 complete potential energy curves at the

MRCI+Q/ASζ level, all bound with respect to ground-state atoms and with binding energies ranging from ~9 to 90 kcal/mol, seems to corroborate the above considerations.

Tables 1 and 2 collect our numerical results (E , r_e , D_e , ω_e , $\omega_e x_e$, α_e , μ , T_e) for 50 bound states of CoO along with existing experimental values for easy comparison, whereas Figure 1 displays full MRCI+Q/ASζ PECs and the corresponding energy level diagram (inset).

1. X⁴Δ. Employing a variety of methods, i.e., MRCI, ACPF, RCCSD(T), and MRCI-L including subvalence (3s²3p⁶) core effects and scalar relativistic corrections (DKH2), we have performed calculations for five low-lying states, X⁴Δ, a⁶Δ, A⁴Σ⁻, B⁴Φ, and C⁴Π, in ascending formal energy order according to the MRCI+Q results; see Table 1. It was not possible to apply the RCCSD(T) method to the B⁴Φ and C⁴Π states. We discuss here separately our findings on the ground state of CoO, followed by the first four excited states and then the rest 45 states, the latter calculated at the plain MRCI+Q/ASζ level.

Including the spin–orbit (SO) coupling the X⁴Δ_Ω splits into four Ω-components, namely, ⁴Δ_{1/2}, ⁴Δ_{3/2}, ⁴Δ_{5/2}, and ⁴Δ_{7/2}, the ground state being ⁴Δ_{7/2, i} (inverted).¹¹ The MRCI/ASζ calculated (experimental)²¹ SO coupling constant A is 181 (162.8 ± 2.60) cm⁻¹.

Table 2. Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal mol⁻¹), Harmonic Frequencies and Anharmonicity Corrections ω_e , $\omega_e x_e$ (cm⁻¹), Rotational–Vibrational Coupling Constants $\alpha_e \times 10^3$ (cm⁻¹), Dipole Moments μ (D), Mulliken Charges on Co q_{Co} , and Energy Separations T_e (cm⁻¹) of 45 Higher States of Co¹⁶O at the MRCI+Q Level of Theory (Experimental Values in Brackets)

| state ^a | $-E$ | r_e | D_e ^b | ω_e | $\omega_e x_e$ | α_e | μ_{FF} ^c | q_{Co} | T_e |
|--|------------|--------------------------------------|--------------------|--------------------------|----------------|------------|-------------------------|----------|---------------------------|
| 1 ² Γ (a ⁴ F) | 1456.79040 | 1.698 | 64.6 | 695 | 4.2 | 4.1 | 4.00 | 0.54 | 8942 |
| 1 ² Π (a ⁴ F) | 1456.78802 | 1.612 | 63.1 | 740 | 9.7 | 7.8 | 4.19 | 0.46 | 9466 |
| 1 ⁴ Γ (a ⁴ F) | 1456.78387 | 1.800 | 60.5 | 607 | 2.6 | 2.8 | 2.23 | 0.65 | 10375 |
| 1 ² Δ (a ⁴ F) | 1456.78072 | 1.699 | 58.5 | 574 | 0.7 | 4.4 | 3.86 | 0.54 | 11068 |
| | | [1.733 ^d] | | | | | | | [10131 ± 5 ^d] |
| 2 ⁴ Δ (a ⁴ F) | 1456.78051 | 1.815 | 58.5 | 556 | 2.6 | 0.5 | 2.27 | 0.66 | 11113 |
| 1 ² Σ ⁺ (a ⁴ F) | 1456.78019 | 1.642 | 58.2 | 711 | 8.1 | 7.2 | 4.35 | 0.50 | 11182 |
| 1 ² Σ ⁻ (a ⁴ F) | 1456.77907 | 1.591 | 57.5 | 570(=ΔG _{1/2}) | | | 3.76 | 0.50 | 11430 |
| 2 ⁴ Π (a ⁴ F) | 1456.77688 | 1.779 | 56.3 | 665 | 20.3 | 2.7 | 2.04 | 0.63 | 11911 |
| 2 ⁴ Σ ⁻ (b ⁴ F) | 1456.77661 | 1.800 | 59.0 | 963 | 32.5 | 1.8 | 3.72 | 0.73 | 11970 |
| 1 ⁶ Π (a ⁴ F) | 1456.77642 | 1.844 | 56.0 | 605 | 3.0 | 2.7 | 2.61 | 0.67 | 12011 |
| 2 ⁴ Φ (a ⁴ F) | 1456.77384 | 1.800 | 54.4 | 535(=ΔG _{1/2}) | | | 4.75 | 0.74 | 12576 |
| 1 ⁶ Γ (a ⁴ F) | 1456.77323 | 1.900 | 53.9 | 583 | 2.3 | 3.5 | 2.86 | 0.69 | 12712 |
| 3 ⁴ Π (a ⁴ F) | 1456.77286 | 1.820 | 53.7 | 639(=ΔG _{1/2}) | | | 4.02 | 0.73 | 12793 |
| 1 ⁶ Σ ⁺ (a ⁴ F) | 1456.77245 | 1.862 | 53.5 | 576 | 3.1 | 2.0 | 2.68 | 0.67 | 12882 |
| 1 ⁴ Σ ⁺ (a ⁴ F) | 1456.77232 | 1.828 | 53.4 | 580 | 2.6 | 2.5 | 2.41 | 0.67 | 12911 |
| 3 ⁴ Δ (a ⁴ F) | 1456.77177 | 1.826 | 53.1 | 549 | 0.8 | 2.3 | 2.47 | 0.67 | 13031 |
| | | [1.778=r ₀ ^e] | | | | | | | [13950.07 ^e] |
| 1 ² Φ (a ⁴ F) | 1456.76846 | 1.627 | 50.9 | 972 | 49.5 | 15.2 | 3.52 | 0.62 | 13758 |
| 2 ² Δ (a ⁴ F) | 1456.76783 | 1.704 | 50.5 | 427 | 2.8 | 4.0 | 3.88 | 0.55 | 13897 |
| 2 ² Σ ⁻ (b ⁴ F) | 1456.76672 | 1.610 | 52.6 | 1054 | 17.2 | 4.4 | 3.50 | 0.54 | 14140 |
| 2 ⁶ Δ (a ⁴ F) | 1456.76667 | 1.910 | 49.8 | 600 | 3.1 | 2.8 | 2.95 | 0.70 | 14150 |
| 1 ⁶ Φ (a ⁴ F) | 1456.76656 | 1.897 | 49.8 | 594 | 3.0 | 2.9 | 2.64 | 0.68 | 14174 |
| 2 ⁶ Π (a ⁴ F) | 1456.76540 | 1.904 | 49.0 | 591 | 2.9 | 2.9 | 2.72 | 0.69 | 14429 |
| 1 ⁶ Σ ⁻ (a ⁴ F) | 1456.76488 | 1.915 | 48.6 | 594 | 3.1 | 2.8 | 2.98 | 0.70 | 14544 |
| 4 ⁴ Π (b ⁴ F) | 1456.76364 | 1.770 | 50.8 | 621 | 3.8 | 2.7 | 3.28 | 0.63 | 14815 |
| | | [1.810=r ₀ ^e] | | | | | | | [15884.64 ^e] |
| 2 ⁴ Γ (b ⁴ F) | 1456.76080 | 1.855 | 48.9 | 640 | 3.4 | 2.8 | 3.50 | 0.66 | 15438 |
| 4 ⁴ Δ (b ⁴ F) | 1456.75855 | 1.796 | 47.5 | 668 | 5.1 | 4.7 | 2.97 | 0.70 | 15932 |
| | | [1.791 ^d] | | [540 ± 10 ^d] | | | | | [15446 ± 8 ^d] |
| | | [1.815=r ₀ ^e] | | | | | | | [15650.679 ^e] |
| 2 ² Π (a ⁴ F) | 1456.75687 | 1.638 | 43.6 | 237(=ΔG _{1/2}) | | | 3.61 | 0.60 | 16302 |
| 2 ⁴ Σ ⁺ (a ⁴ F) | 1456.75524 | 1.845 | 42.7 | 621 | 2.9 | 2.8 | 3.02 | 0.66 | 16660 |
| 2 ² Φ (a ⁴ F) | 1456.75419 | 1.772 | 42.0 | 952 | 18.2 | -0.7 | 1.96 | 0.63 | 16890 |
| 3 ² Π (a ⁴ F) | 1456.75091 | 1.717 | 39.9 | 846 | 22.1 | -3.1 | 2.68 | 0.62 | 17610 |
| 3 ² Δ (a ⁴ F) | 1456.74751 | 1.642 | 37.8 | 869 | 0.3 | 2.5 | 2.51 | 0.52 | 18355 |
| 4 ² Π (b ⁴ F) | 1456.74571 | 1.663 | 39.5 | 1118 | 43.9 | 3.7 | 3.65 | 0.57 | 18750 |
| 2 ² Σ ⁺ (a ⁴ F) | 1456.74358 | 1.643 | 35.3 | 728 | -3.0 | 2.8 | 2.37 | 0.53 | 19219 |
| 3 ⁴ Φ (b ⁴ F) | 1456.74267 | 1.904 | 37.6 | 595 | 3.0 | 2.8 | 2.39 | 0.68 | 19418 |
| | | [1.845 ^e] | | | | | | | [21046 ^e] |
| 5 ⁴ Π (b ⁴ F) | 1456.74161 | 1.910 | 36.9 | 593 | 3.0 | 2.8 | 2.46 | 0.69 | 19650 |
| 5 ² Π (b ⁴ F) | 1456.73708 | 1.693 | 34.0 | 730 | -8.2 | 3.6 | 2.63 | 0.55 | 20645 |
| 3 ⁶ Δ (a ⁴ F) | 1456.73559 | 1.855 | 30.4 | 634 | 3.9 | 3.2 | 2.65 | 0.76 | 20971 |
| 3 ² Φ (b ⁴ F) | 1456.73546 | 1.666 | 33.0 | 746 | -2.3 | 6.4 | 3.73 | 0.54 | 21000 |
| 4 ² Δ (b ⁴ F) | 1456.73395 | 1.661 | 32.0 | 830 | 9.5 | 5.3 | 1.86 | 0.59 | 21332 |
| 2 ⁶ Φ (a ⁴ F) | 1456.73123 | 1.865 | 27.7 | 600 | 3.4 | 3.3 | 2.77 | 0.77 | 21928 |
| 3 ⁶ Π (a ⁴ F) | 1456.72993 | 1.830 | 26.8 | 585 | 2.8 | 4.0 | 2.59 | 0.75 | 22215 |
| 2 ⁶ Σ ⁻ (b ⁴ F) | 1456.72355 | 1.874 | 25.5 | 572 | 3.6 | 2.9 | 2.92 | 0.79 | 23615 |
| 4 ⁶ Π (b ⁴ F) | 1456.72230 | 1.863 | 24.8 | 659 | 3.8 | 2.7 | 2.54 | 0.68 | 23889 |
| 2 ⁶ Σ ⁺ (a ⁴ F) | 1456.71952 | 1.806 | 20.3 | 703 | 5.0 | 4.1 | 2.21 | 0.62 | 24498 |
| 4 ⁶ Δ (b ⁴ F) | 1456.69501 | 1.920 | 7.8 | 589 | 3.0 | 2.9 | 2.96 | 0.69 | 29877 |

^aFor MRCI results see Table S1 of Supporting Information, ref 50. ^bWith respect to adiabatic products; in parentheses the adiabatic atomic terms of the Co atom. ^cDipole moments calculated with the finite field method. ^dReference 19. ^eReference 16.

At the highest level of theory and in all methods MRCI+DKH2+Q (C-MRCI+DKH2+Q) [C-ACPF+DKH2]{C-RCCSD(T)+DKH2}|MRCI-L+DKH2+Q], the bond distance,

$r_e = 1.607$ (1.606) [1.603] {1.611} |1.609| Å, is essentially method independent; Table 1. Disregarding the 1.603 value, $r_e = 1.609 \pm 0.002$ Å at this level of theory, in fair agreement with the

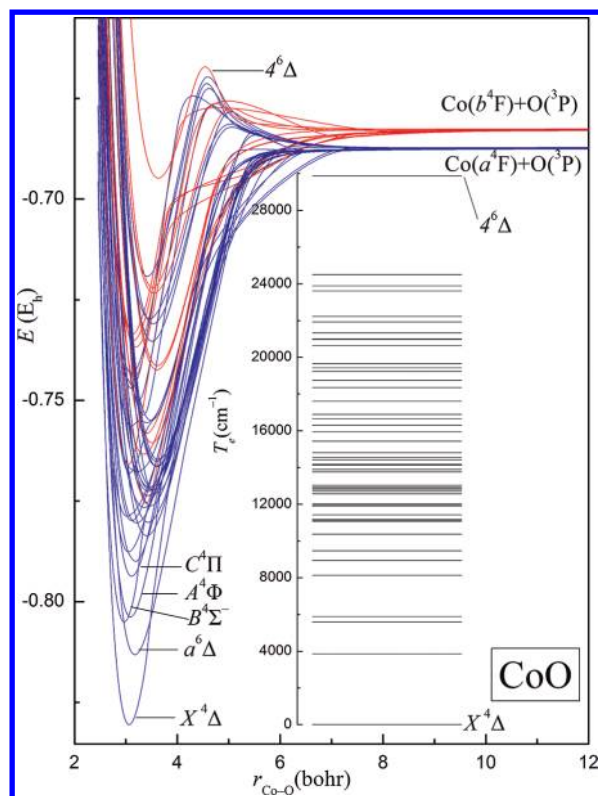


Figure 1. MRCI+Q/AS ζ adiabatic PECs and energy level diagram (inset) of 50 (=36 from the first +14 from the second channel) bound states of CoO. The ordering follows that of Tables 1 and 2. All energies are shifted by +1456 E $_h$.

experimental value of 1.627 862(1) Å.²¹ Observe that without the relativistic effects amounting in all methods to a shortening of ~ 0.01 Å, the calculated bond length is close to 1.620 Å in good agreement with experiment. The best agreement is obtained at the C-RCCSD(T) level where $r_e = 1.625$ Å. Worth noticing as well is the fact that the core subvalence ($3s^2 3p^6$) electrons have practically no effect on the bond length. The corresponding dissociation energy values are $D_e = 86.0$ (84.4) [84.8] {88.9} {87.1} kcal/mol, where combined core + relativistic effects reduce the D_e by ~ 1 kcal/mol. The zero point energy correction ($=\omega_e/2$) reduces the above D_e values by ~ 1.3 kcal/mol, giving a multireference estimated $D_0^0 = 85$ –86 kcal/mol. The best result, as compared to the experimental value, is obtained at the C-RCCSD(T) approach, where $D_0^0 = 89.0$ kcal/mol; Table 1. Even so, the difference between experiment ($D_0^0 = 94.1 \pm 2.1$ kcal/mol²⁰) and theory is considerable, the former being larger by ~ 8 kcal/mol (or $\sim 10\%$) from the estimated multireference value of 85–86 kcal/mol. Because the one-electron basis set is certainly adequate and the combined core and relativistic effects are of minor importance, the discrepancies observed are mainly due to missing electron correlation.

We turn now to the calculation of the dipole moment of the $X^4\Delta$ state. With the exception of the MRCI-L type calculations, dipole moments obtained by the expectation value method range from $\langle \mu \rangle = 3.3$ to 3.6 D, with corresponding finite field values $\mu_{FF} = 4.4$ –4.8 D, the latter being the most reliable.⁴⁵ On the other hand, the MRCI-L $\langle \mu \rangle$ and μ_{FF} values at all levels are practically equal, indicating a better internal consistency of the MRCI-L type calculations. The recommended value for the dipole moment of CoO is $\mu(X^4\Delta) = 4.5 \pm 0.1$ D; recall that the dipole moment of CoO has not been measured yet.

We examine now the bonding character of the $X^4\Delta$ state. The leading equilibrium MRCI configuration and Mulliken atomic populations, suppressing the 20 internal electrons, are

$$|X^4\Delta\rangle_{A_1} \approx 0.82|1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^2 1\delta_-^1\rangle$$

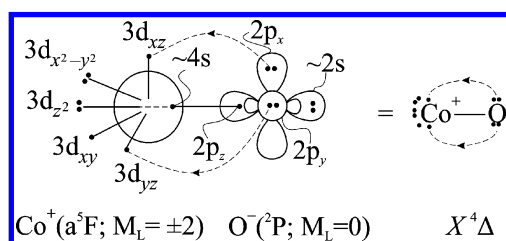
$$4s^{1.08} 4p_z^{0.12} 4p_x^{0.04} 4p_y^{0.04} 3d_{z^2}^{1.49} 3d_{xz}^{1.34} 3d_{yz}^{1.34} 3d_{x^2-y^2}^{1.98} 3d_{xy}^{1.01} /_{Co}$$

$$2s^{1.89} 2p_z^{1.38} 2p_x^{1.60} 2p_y^{1.60} /_{O}$$

Some 0.6 e $^-$ are transferred from the Co to the O atom. Taking also into account the synthesis of the MRCI σ -orbitals, i.e., $1\sigma = 2s$, $2\sigma \approx (0.47)3d_{z^2} + (0.32)4s - (0.78)2p_z$, and

$$3\sigma \approx (0.66)4s - (0.72)3d_{z^2} - (0.20)2p_z$$

the following vbL (valence–bond–Lewis) icon can be considered as a fair representation of the bonding within the Co $^+$ O $^-$ ionic model.



According to the Mulliken populations, about 0.8 e $^-$ are transferred from the O $^-$ to Co $^+$ through the π -system, while ~ 0.3 e $^-$ are moving back through the σ frame. Certainly the bonding is more involved, but we believe that the picture above represents a good “zeroth-order” approximation of the attractive interaction between Co(a^4F) + O(3P).

2. $^6\Delta$, $^4\Sigma^-$, $^4\Phi$, $^4\Pi$. Experimentally, the first three excited states of CoO, $^4\Sigma^-$, $^4\Pi_{5/2}$, and $^6\Delta$ are within 7000 cm $^{-1}$, with energy distances with respect to the $X^4\Delta_{7/2}$, $T = 3390$, 5837, and 7028 cm $^{-1}$, respectively, the $^4\Sigma^-$ being the first excited state.¹⁹ However, for both $^4\Sigma^-$ and $^6\Delta$ states, T and r_e values are not certain; bond lengths have been obtained via the Herschbach–Laurie⁴⁶ semiempirical linear regression approach (see ref 19 for details). It should be stated also that a low-lying $^4\Phi$ state at $T \sim 5000$ cm $^{-1}$, calculated here for the first time (Table 1 and Figure 2), has never been observed.

For the states above subvalence core and scalar relativistic effects are not significant. For instance, for the $^6\Delta$ state the bond distance is reduced by about 0.002 and 0.006 Å due to core and relativistic effects, respectively, whereas core effects alone increase T_e values by 200–300 cm $^{-1}$ depending on the method employed; see Table 1. Results of similar absolute size hold for the other three states, $^4\Sigma^-$, $^4\Phi$, and $^4\Pi$. Therefore, MRCI-L +DKH2+Q (+core corrections) energy separation estimates are as follows: $T = 4104(+300) \simeq 4400$ cm $^{-1}$ ($^6\Delta$), 5016(–100) \simeq 4900 cm $^{-1}$ ($^4\Phi$), 5300(–200) \simeq 5100 cm $^{-1}$ ($^4\Sigma^-$), and 7304(–200) \simeq 7100 cm $^{-1}$ ($^4\Pi$). The calculated SO coupling constants $|A|$ of $a^6\Delta$, $A^4\Phi$, and $C^4\Pi$ states are 117, 170, and 178 cm $^{-1}$, respectively. Experimentally, $A = -158.5723(21)$ cm $^{-1}$ for the $C^4\Pi$ state,¹⁴ i.e., the $\Lambda + \Sigma = 5/2$ component is the lowest one. Taking into account the SO coupling for the $C^4\Pi$ and the zero-point energy corrections, the previous energy separations with respect to the $X^4\Delta$ become $T_0 = T_e - \Delta\omega_e/2 = 4300$ ($a^6\Delta \leftarrow X^4\Delta$), 5638 ($^4\Sigma^- \leftarrow X^4\Delta_{7/2}$), and 7314 ($^4\Pi_{5/2} \leftarrow X^4\Delta_{7/2}$) cm $^{-1}$; see Figure 2. There is an obvious disagreement between theory and experiment, the latter values being¹⁹ $T = 7028$ ($^6\Delta$), 3390 ($^4\Sigma^-$), and 5837 ($^4\Pi_{5/2}$) cm $^{-1}$. Recall, however, that

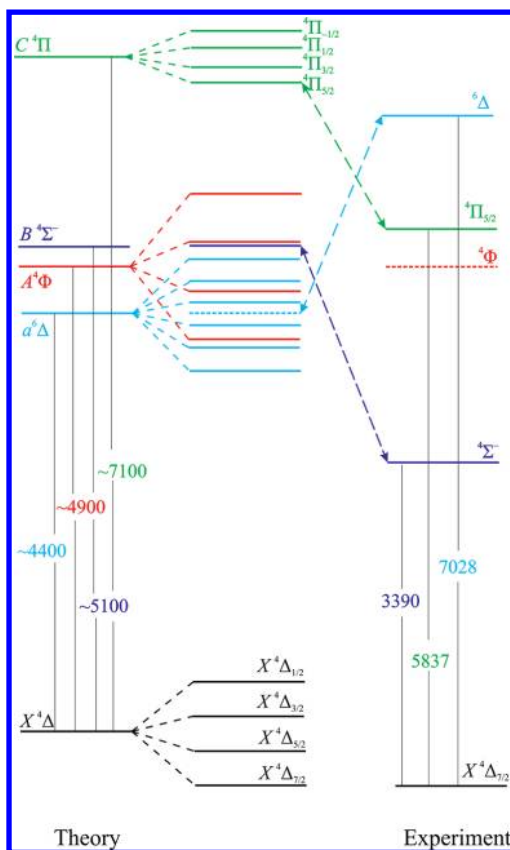


Figure 2. Theoretical vs experimental energy separation values (cm^{-1}) of the first five low-lying states of CoO including SO coupling. The ${}^4\Phi$ state has not been observed experimentally. The $\Omega = \Lambda + \Sigma$ components of the ${}^4\Phi_{\Omega}$ and ${}^6\Delta_{\Omega}$ states are (9/2, 7/2, 5/2, and 3/2) and (9/2, 7/2, 5/2, 3/2, 1/2, and -1/2), respectively.

the experimental T values for the ${}^6\Delta$ and ${}^4\Sigma^-$ states are quite uncertain (vide supra). Therefore, and according to our calculations, the first four excited states of CoO can be tentatively labeled, as $a^6\Delta$, $A^4\Phi$, $B^4\Sigma^-$, and $C^4\Pi$.

Considering that the subvalence core effects are of no importance, the MRCI-L+DKH2+Q bond lengths (experimental values in parentheses¹⁹) are $r_e = 1.667(1.686)$, 1.628 , $1.578(1.641)$, and $1.638(1.653)$ Å, for the $a^6\Delta$, $A^4\Phi$, $B^4\Sigma^-$, and $C^4\Pi$ states, respectively; Table 1. With the exception of the ${}^4\Sigma^-$ state, where the r_e value is calculated to be 0.06 Å shorter, the agreement between theory and experiment can be considered as good. As was already stated, however, experimental r_e values for the ${}^6\Delta$ and ${}^4\Sigma^-$ states are uncertain by at least ± 0.01 Å (vide supra). Recommended dipole moments based on the MRCI-L+DKH2+Q finite field approach are $\mu_{\text{FF}} = 1.8$ ($a^6\Delta$), 5.8 ($A^4\Phi$), 5.2 ($B^4\Sigma^-$), and 5.5 ($C^4\Pi$) D; Table 1.

We would like now to touch upon the electronic structure of these states. In what follows, we give the dominant equilibrium MRCI configurations along with corresponding Mulliken atomic populations.

$$|a^6\Delta\rangle_{A_1} \approx 0.84|1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^2 1\delta_-^1\rangle$$

$$4s^{0.90} 4p_z^{0.33} 4p_x^{0.03} 4p_y^{0.03} 3d_z^{1.25} 3d_{xz}^{1.43} 3d_{yz}^{1.43} 3d_{x^2-y^2}^{1.96} 3d_{xy}^{1.02} / 2s^{1.94} 2p_z^{1.55} 2p_x^{1.51} 2p_y^{1.51}$$

$$|B^4\Sigma^-\rangle \approx 0.81|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^2 1\delta_-^2\rangle$$

$$4s^{0.85} 4p_z^{0.12} 4p_x^{0.04} 4p_y^{0.04} 3d_z^{1.04} 3d_{xz}^{1.33} 3d_{yz}^{1.33} 3d_{x^2-y^2}^{1.80} 3d_{xy}^{1.80} / 2s^{1.89} 2p_z^{1.10} 2p_x^{1.78} 2p_y^{1.78}$$

$$|A^4\Phi\rangle_{B_1} \approx 0.56|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^2 2\pi_y^1 1\delta_+^2 1\delta_-^1\rangle$$

$$- 0.56|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^2 1\delta_+^1 1\delta_-^2\rangle$$

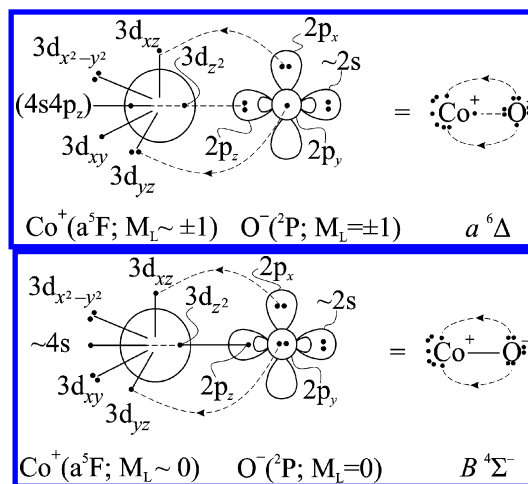
$$4s^{0.88} 4p_z^{0.14} 4p_x^{0.05} 4p_y^{0.05} 3d_z^{1.03} 3d_{xz}^{1.58} 3d_{yz}^{1.57} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.49} / 2s^{1.90} 2p_z^{1.04} 2p_x^{1.84} 2p_y^{1.84}$$

Changing the leading coefficient(s), 0.56, of the $A^4\Phi$ state, to 0.51 and the plus sign to minus, we obtain the $C^4\Pi$ state with very similar populations to those of the $A^4\Phi$ state. Overall, about 0.6 and 0.7 e^- are moving from Co to O in ($a^6\Delta$, $B^4\Sigma^-$) and ($A^4\Phi$, $C^4\Pi$) states, respectively. Based on the leading configurations, atomic populations, and taking into consideration the synthesis of the σ atomic orbitals of the $a^6\Delta$ and $B^4\Sigma^-$ states, namely

$$a^6\Delta \begin{cases} 2\sigma \approx (0.42)3d_{z^2} - (0.82)2p_z \\ 3\sigma \approx (0.90)3d_{z^2} + (0.41)2p_z \\ 4\sigma \approx (0.90)4s - (0.49)4p_z \end{cases}$$

$$B^4\Sigma^- \begin{cases} 2\sigma \approx (0.58)3d_{z^2} - (0.72)2p_z \\ 3\sigma \approx (0.85)4s - (0.47)3d_{z^2} \end{cases}$$

the bonding of these two states can be visualized by the two vbl diagrams below.



The bonding of the $A^4\Phi$, $C^4\Pi$ states is more involved and will not be discussed at this point.

3. Higher States. Table 2 collects results for 45 higher bound states of CoO, all calculated at the MRCI(+Q)/AS ζ level of theory, lying within an energy range of $21\,000\text{ cm}^{-1}$. To the $\text{Co}(a^4F) + \text{O}(^3P)$ channel correlate adiabatically 31 states, the rest 14 to $\text{Co}(b^4F) + \text{O}(^3P)$; see Figure 1. Experimental results exist for five states, ${}^2\Delta$, ${}^4\Delta[2]$, ${}^4\Pi$, and ${}^4\Phi$, located between $T = 10\,000$ and $21\,000\text{ cm}^{-1}$. These can be identified with the calculated ones ${}^1\Delta$, ${}^3\Delta$, ${}^4\Pi$, ${}^4\Delta$, and ${}^3\Phi$ as labeled in Table 2. Given the inherent egregiousness of the CoO molecule, the agreement between experiment and theory can be considered as good, with differences in the energy separation values T no more

than 1000 cm^{-1} , or about 10%. We were unable to locate one more state of ${}^4\Phi$ symmetry detected experimentally¹⁶ at $T = 16\,000\text{ cm}^{-1}$. All 50 states studied have a strong component of ionic character with increasing ionicity for states of higher multiplicity. In particular, the average Mulliken positive charge on Co (\bar{q}_{Co}) for 17 doublets, 18 quartets, and 15 sextets is $\bar{q}_{\text{Co}} = 0.55, 0.67,$ and 0.70 , respectively. A similar tendency has been observed in the FeO molecule as well.³

MRCI results for the 45 higher states of CoO are given in Table S1 in the Supporting Information. In addition, for these states MRCI leading configurations and atomic populations are available in Tables S2 and S3, respectively, in the Supporting Information.⁵⁰

B. CoO^+ . The ground state of Co^+ is ${}^3\text{F}(3\text{d}^8)$ with its first excited state ${}^5\text{F}(4\text{s}^13\text{d}^7)$ located 0.4287 eV higher.⁴³ The interaction of $\text{Co}^+({}^3\text{F}) + \text{O}({}^3\text{P})$ related to the first channel results in 36 molecular $2\text{S}+1\Lambda$ states, singlets, triplets, and quintets, that is, ${}^{1,3,5}(\Sigma^+[2], \Sigma^-, \Pi[3], \Delta[3], \Phi[2], \Gamma)$. Another set of 36 states of the same orbital angular momentum are obtained from the second channel (${}^5\text{F}$), but with multiplicities $2\text{S} + 1 = 3, 5, 7$. We have constructed full MRCI+Q/AS ζ PECs for all singlets (11 bound + 1 repulsive), 8 triplets, and 8 quintets, i.e., ${}^{3,5}(\Sigma^+, \Sigma^-, \Pi[2], \Delta[2], \Phi, \Gamma)$, all correlating adiabatically to the lowest channel $\text{Co}({}^3\text{F}) + \text{O}({}^3\text{P})$. Their MRCI+Q/AS ζ PECs are displayed in Figure 3. From the second channel, $\text{Co}^+({}^5\text{F}) + \text{O}({}^3\text{P})$, we have calculated MRCI+Q/AS ζ PECs for all 12 septets 4 of which can be considered as bound; see Figure 3. The remaining 8 septets are of repulsive nature, displayed also in Figure 3. As was discussed earlier, Nakao and co-workers³⁰ studied

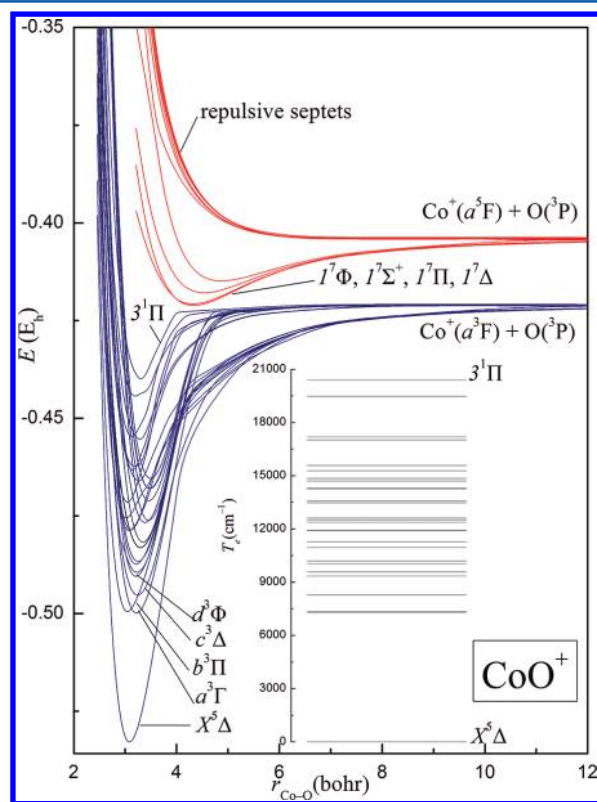


Figure 3. MRCI+Q/AS ζ adiabatic PECs and energy level diagram (inset) of 27 bound states of CoO^+ correlating to $\text{Co}^+({}^3\text{F}) + \text{O}({}^3\text{P})$. The ordering follows that of Tables 3 and 4. All energies are shifted by $+1456\text{ E}_h$. Twelve more PECs of 4 bound ${}^7(\Phi, \Sigma^+, \Pi, \Delta)$ and 8 repulsive states correlating to ${}^5\text{F} + {}^3\text{P}$ are also shown.

around equilibrium the exact same 8 triplets and 8 quintets as in the present work; for some reason, no singlets have been calculated. Their results are contrasted with ours in Tables 3 and 4.

For the first 5 states ($X^5\Delta, a^3\Gamma, b^3\Pi, c^3\Delta, d^3\Phi$) the methods employed at the highest level are C-MRCI+DKH2+Q and MRCI-L+DKH2+Q, whereas for the X-state alone the highest level includes the C-ACPF-DKH2+Q and C-RCCSD(T)+DKH2 methods as well; Table 3. The higher 26 states are calculated at the plain MRCI(+Q) level; Table 4.

1. $X^5\Delta$. The ground-state symmetry of CoO^+ , $X^5\Delta_4$, was determined experimentally only recently²⁷ and confirmed theoretically for the first time by Nakao and co-workers.³⁰ The present high-level calculations leave no doubt as to the symmetry (${}^5\Delta$) of the lowest state of CoO^+ , with the first excited state $a^3\Gamma$ some 7500 cm^{-1} higher (vide infra). It can be seen from Table 3 that, in all methods, core-correlation ($3\text{s}^23\text{p}^6$) and scalar relativistic effects reduce the bond distance by the same amount, $\sim 0.01\text{ \AA}$, the combined effect being -0.016 \AA and to an excellent approximation additive. Corresponding effects on the binding energy are very close to -3.5 and $+6.5\text{ kcal/mol}$, respectively, the combined effect, also additive, being $\sim 3\text{ kcal/mol}$. Similar conclusions hold for the next 4 states. Thus, our recommended MRCI-L+DKH2+Q r_e and D_e (D_0) values are $r_e = 1.626 - 0.008$ (core effects) $= 1.618\text{ \AA}$ and $D_e = 76.5 - 3.7 = 72.8$ (71.6) kcal/mol , in fair agreement to the experimental values of $r_0 = 1.65 \pm 0.01\text{ \AA}$ ²⁷ and $D_0^0 = 75.9 \pm 1.4\text{ kcal/mol}$.¹² The experimental ionization energy of CoO is $\text{IE} = 8.69 \pm 0.20\text{ eV}$,¹² in good agreement at the highest level(s) of calculation C-MRCI+DKH2+Q(C-RCCSD(T)+DKH2)[MRCI-L+DKH2+Q] $= 8.19$ (8.67) [8.42] eV .

The main MRCI equilibrium configuration and the atomic Mulliken populations are

$$|X^5\Delta\rangle_A \approx 0.86|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^1 1\delta_-^1\rangle$$

$$4\text{s}^{0.30} 4\text{p}_z^{0.06} 4\text{p}_x^{0.02} 4\text{p}_y^{0.02} 3\text{d}_{z^2}^{1.23} 3\text{d}_{xz}^{1.51} 3\text{d}_{yz}^{1.51} 3\text{d}_{x^2-y^2}^{1.96} 3\text{d}_{xy}^{1.01}$$

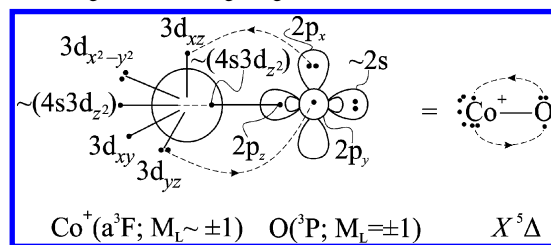
$$/2\text{s}^{1.93} 2\text{p}_z^{1.45} 2\text{p}_x^{1.43} 2\text{p}_y^{1.43}$$

In conjunction with the composition of the 2σ and 3σ equilibrium orbitals (the 1σ is a pure 2s orbital on oxygen),

$$2\sigma \approx (0.47)3\text{d}_{z^2} - (0.81)2\text{p}_z + (0.22)4\text{s},$$

$$3\sigma \approx (0.85)3\text{d}_{z^2} + (0.40)2\text{p}_z - (0.28)4\text{s}$$

the following vBL bonding diagram can be drawn



The bonding implicates $3e^-$ along the σ -frame, $(4\text{s}3\text{d}_{z^2})^{1.5} + (2\text{p}_z)^{1.5}$, slightly assisted through the interaction of the π -system. Near 0.4 e^- are moving from Co^+ to O via the σ path, while 0.1 e^- are moving back via the π path from O to Co^+ , resulting in a total Co^+ to O transfer of 0.3 e^- . The calculated SO coupling constant A of $X^5\Delta$ state is $A = -143\text{ cm}^{-1}$, negative according to ref 27.

2. $a^3\Gamma, b^3\Pi, c^3\Delta, d^3\Phi$. Results of the above 4 states have been obtained at the MRCI(MRCI-L) methodology including core + scalar relativistic corrections; Table 3. All four states are of intense multireference character, hence any single-reference calculation

Table 3. Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal mol⁻¹), Harmonic Frequencies and Anharmonicity Corrections ω_e , $\omega_e x_e$ (cm⁻¹), Rotational–Vibrational Coupling Constants $\alpha_e \times 10^3$ (cm⁻¹), Mulliken Charges on Co q_{Co} , and Energy Separations T_e (cm⁻¹) of the First Five States of Co¹⁶O⁺

| method ^a | $-E$ | r_e | D_e^b | ω_e | $\omega_e x_e$ | α_e | q_{Co} | T_e |
|---------------------|------------|---------------------|--|------------|----------------|------------|----------|-------|
| | | | X⁵Δ (a³F) | | | | | |
| MRCI | 1456.49423 | 1.635 | 66.8 | 833 | 4.7 | 4.2 | 1.32 | 0.0 |
| MRCI+Q | 1456.53335 | 1.630 | 70.3 | 852 | 5.0 | 4.2 | | 0.0 |
| MRCI+DKH2 | 1466.98425 | 1.626 | 73.6 | 847 | 5.8 | 4.4 | | 0.0 |
| MRCI+DKH2+Q | 1467.02360 | 1.620 | 77.0 | 868 | 6.2 | 4.4 | | 0.0 |
| C-MRCI | 1456.90512 | 1.631 | 62.6 | 839 | 5.1 | 4.4 | | 0.0 |
| C-MRCI+Q | 1456.98709 | 1.622 | 66.6 | 871 | 5.7 | 4.4 | | 0.0 |
| C-MRCI+DKH2 | 1467.39598 | 1.623 | 69.4 | 854 | 6.4 | 4.6 | | 0.0 |
| C-MRCI+DKH2+Q | 1467.47828 | 1.613 | 73.4 | 890 | 7.2 | 4.5 | | 0.0 |
| ACPF | 1456.53263 | 1.631 | 70.8 | 847 | 5.1 | 4.2 | | 0.0 |
| ACPF+DKH2 | 1467.02293 | 1.621 | 77.4 | 863 | 6.3 | 4.4 | | 0.0 |
| C-ACPF | 1456.99412 | 1.624 | 67.5 | 865 | 5.8 | 4.5 | | 0.0 |
| C-ACPF+DKH2 | 1467.48543 | 1.615 | 73.8 | 884 | 7.3 | 4.6 | | 0.0 |
| RCCSD(T) | 1456.54162 | 1.631 | 67.6 | 832 | 3.5 | 3.8 | | 0.0 |
| RCCSD(T)+DKH2 | 1467.03192 | 1.620 | 74.1 | 846 | 3.7 | 3.9 | | 0.0 |
| C-RCCSD(T) | 1457.01610 | 1.626 | 64.7 | 843 | 4.2 | 4.1 | | 0.0 |
| C-RCCSD(T)+DKH2 | 1467.50724 | 1.615 | 71.2 | 861 | 4.4 | 4.1 | | 0.0 |
| MRCI-L | 1456.51225 | 1.643 | 74.0 | 807 | 3.1 | 3.4 | 1.29 | 0.0 |
| MRCI-L+Q | 1456.53707 | 1.638 | 70.5 | 816 | 3.1 | 3.5 | | 0.0 |
| MRCI-L+DKH2 | 1467.00206 | 1.631 | 81.0 | 811 | 2.7 | 3.7 | | 0.0 |
| MRCI-L+DKH2+Q | 1467.02716 | 1.626 | 76.5 | 822 | 2.7 | 3.8 | | 0.0 |
| MRCI+Q ^c | | 1.623 | 78.6 | 881 | | | | |
| expt | | 1.65 ± 0.01^{d} | 75.9 ± 1.4^e | | | | | |
| | | | a³Γ (a³F) | | | | | |
| MRCI | 1456.46375 | 1.712 | 47.7 | 681 | 1.9 | 3.4 | 1.37 | 6689 |
| MRCI+Q | 1456.50016 | 1.701 | 49.5 | 688 | 1.6 | 3.5 | | 7283 |
| MRCI+DKH2 | 1466.95402 | 1.704 | 54.6 | 682 | 2.1 | 3.5 | | 6636 |
| MRCI+DKH2+Q | 1466.99068 | 1.694 | 56.3 | 690 | 1.7 | 3.6 | | 7226 |
| C-MRCI | 1456.87545 | 1.709 | 44.0 | 672 | 1.7 | 3.6 | | 6513 |
| C-MRCI+Q | 1456.95404 | 1.692 | 45.9 | 681 | 1.1 | 3.8 | | 7253 |
| C-MRCI+DKH2 | 1467.36665 | 1.699 | 51.0 | 674 | 2.0 | 3.8 | | 6438 |
| C-MRCI+DKH2+Q | 1467.44561 | 1.685 | 52.9 | 685 | 1.4 | 4.0 | | 7170 |
| MRCI-L | 1456.47892 | 1.712 | 53.5 | 697 | 3.5 | 2.7 | 1.34 | 7313 |
| MRCI-L+Q | 1456.50246 | 1.701 | 48.5 | 704 | 3.4 | 3.3 | | 7596 |
| MRCI-L+DKH2 | 1466.96904 | 1.704 | 60.0 | 692 | 3.5 | 3.0 | | 7248 |
| MRCI-L+DKH2+Q | 1466.99282 | 1.693 | 55.0 | 698 | 3.5 | 3.4 | | 7537 |
| MRCI+Q ^c | | 1.706 | 57.4 | 723 | | | | |
| | | | b³Π (a³F) | | | | | |
| MRCI | 1456.46058 | 1.628 | 45.6 | 665 | 3.7 | 8.0 | 1.27 | 7385 |
| MRCI+Q | 1456.49991 | 1.607 | 49.3 | 758 | 4.2 | 8.3 | | 7339 |
| MRCI+DKH2 | 1466.95137 | 1.629 | 52.8 | 658 | 3.2 | 6.8 | | 7216 |
| MRCI+DKH2+Q | 1466.99059 | 1.605 | 56.2 | 731 | 4.4 | 7.9 | | 7245 |
| C-MRCI | 1456.87273 | 1.619 | 42.0 | 687 | 5.1 | 8.3 | | 7110 |
| C-MRCI+Q | 1456.95553 | 1.592 | 46.5 | 823 | 4.8 | 9.3 | | 6927 |
| C-MRCI+DKH2 | 1467.36424 | 1.620 | 49.3 | 672 | 5.6 | 7.7 | | 6965 |
| C-MRCI+DKH2+Q | 1467.44695 | 1.591 | 53.4 | 790 | 5.2 | 8.9 | | 6876 |
| MRCI-L | 1456.47407 | 1.614 | 50.4 | 641 | 3.7 | 7.9 | 1.25 | 8378 |
| MRCI-L+Q | 1456.50012 | 1.597 | 47.0 | 769 | 3.7 | 8.4 | | 8109 |
| MRCI-L+DKH2 | 1466.96440 | 1.625 | 57.0 | 771 | 3.8 | 8.8 | | 8265 |
| MRCI-L+DKH2+Q | 1466.99016 | 1.600 | 53.2 | 751 | 3.9 | 7.4 | | 8122 |
| MRCI+Q ^c | | 1.648 | 55.1 | 622 | | | | |
| | | | c³Δ (a³F) | | | | | |
| MRCI | 1456.45879 | 1.729 | 44.6 | 634 | 1.6 | 2.4 | 1.37 | 7779 |
| MRCI+Q | 1456.49556 | 1.715 | 46.6 | 632 | 0.6 | 2.4 | | 8293 |
| MRCI+DKH2 | 1466.94905 | 1.721 | 51.5 | 630 | 1.5 | 2.4 | | 7725 |
| MRCI+DKH2+Q | 1466.98610 | 1.706 | 53.5 | 628 | 0.4 | 2.5 | | 8231 |
| C-MRCI | 1456.87019 | 1.727 | 40.7 | 622 | 1.4 | 2.5 | | 7667 |
| C-MRCI+Q | 1456.94905 | 1.705 | 42.7 | 615 | -0.5 | 2.8 | | 8349 |

Table 3. continued

| method ^a | $-E$ | r_e | D_e^b | ω_e | $\omega_e x_e$ | α_e | q_{Co} | T_e |
|---------------------|------------|-------|--------------------------------|------------|----------------|------------|----------|-------|
| | | | $c^3\Delta$ (a ³ F) | | | | | |
| C-MRCI+DKH2 | 1467.36141 | 1.718 | 47.7 | 618 | 1.3 | 2.7 | | 7588 |
| C-MRCI+DKH2+Q | 1467.44068 | 1.695 | 49.8 | 612 | -0.8 | 3.0 | | 8253 |
| MRCI-L | 1456.47495 | 1.724 | 50.8 | 650 | 2.1 | 2.0 | 1.33 | 8184 |
| MRCI-L+Q | 1456.49859 | 1.710 | 46.0 | 649 | 1.7 | 2.1 | | 8444 |
| MRCI-L+DKH2 | 1466.96500 | 1.715 | 57.5 | 640 | 1.8 | 1.7 | | 8135 |
| MRCI-L+DKH2+Q | 1466.98892 | 1.700 | 52.4 | 638 | 2.6 | 2.3 | | 8393 |
| MRCI+Q ^c | | 1.715 | 55.5 | 672 | | | | |
| | | | $d^3\Phi$ (a ³ F) | | | | | |
| MRCI | 1456.45419 | 1.707 | 41.6 | 663 | 1.2 | 4.1 | 1.32 | 8788 |
| MRCI+Q | 1456.49078 | 1.694 | 43.6 | 685 | 2.4 | 4.7 | | 9341 |
| MRCI+DKH2 | 1466.94653 | 1.690 | 49.8 | 678 | 2.5 | 4.6 | | 8279 |
| MRCI+DKH2+Q | 1466.98352 | 1.681 | 51.8 | 702 | 3.3 | 5.0 | | 8798 |
| C-MRCI | 1456.86540 | 1.704 | 37.4 | 652 | 1.7 | 4.7 | | 8719 |
| C-MRCI+Q | 1456.94441 | 1.684 | 39.5 | 680 | 2.1 | 5.2 | | 9368 |
| C-MRCI+DKH2 | 1467.35866 | 1.687 | 45.8 | 668 | 2.7 | 5.1 | | 8190 |
| C-MRCI+DKH2+Q | 1467.43825 | 1.670 | 48.0 | 704 | 3.7 | 5.5 | | 8785 |
| MRCI-L | 1456.46853 | 1.718 | 46.9 | 661 | 1.8 | 3.7 | 1.31 | 9594 |
| MRCI-L+Q | 1456.49208 | 1.704 | 41.7 | 678 | 4.3 | 3.3 | | 9874 |
| MRCI-L+DKH2 | 1466.96066 | 1.700 | 54.8 | 669 | 2.6 | 4.0 | | 9087 |
| MRCI-L+DKH2+Q | 1466.98466 | 1.688 | 49.7 | 681 | 2.8 | 4.4 | | 9328 |
| MRCI+Q ^c | | 1.706 | 51.7 | 705 | | | | |

^aSee Table 1 for explanation of acronyms and symbols. ^bWith respect to the adiabatic fragments; term in parentheses after the molecular term symbol denotes the end term symbol of Co⁺. ^cReference 30; MRCI+Q/[6s5p3d1f/c₀aug-cc-pVTZ/o] with Stuttgart relativistic small core (1s²2s²2p⁶/c₀) effective potential; D_0 values. ^dReference 27; r_0 value. ^eReference 12; D_0 value.

approach was precluded (see Tables S4, S5, and S6 of the Supporting Information for plain MRCI results, leading MRCI configurations, and atomic populations, respectively).⁵⁰ The first two states, a³Γ and b³Π, well separated from the X⁵Δ state, are energetically close, with C-MRCI+DKH2+Q (MRCI-L+DKH2+Q) $T_e = 7170$ (7537) and 6876 (8122) cm⁻¹, respectively. With some confidence, we can claim that a³Γ is the first excited state of CoO⁺ with the b³Π about 500 cm⁻¹ higher; see Table 3 and Figure 3. The corresponding T_e values for the c³Δ and d³Φ are $T_e = 8253$ (8393) and 8785 (9328) cm⁻¹, respectively. As in the X⁵Δ state, core and relativistic effects separately reduce the bond distance by the same amount (~0.01 Å), whereas core (relativistic) effects decrease (increase) binding energies by ~3 (7) kcal/mol, both effects being well additive. Therefore, recommended r_e and D_e values at the MRCI-L+DKH2+Q level corrected for core effects are $r_e = 1.693 - 0.09 = 1.684$ (a³Γ), $1.600 - 0.015 = 1.585$ (b³Π), $1.700 - 0.01 = 1.690$ (c³Δ), $1.688 - 0.01 = 1.678$ (d³Φ) Å, and $D_e = 55.0 - 3.6 = 51.4$ (a³Γ), $53.2 - 2.8 = 50.4$ (b³Π), $52.4 - 3.9 = 48.5$ (c³Δ), $49.7 - 4.1 = 45.6$ (d³Φ) kcal mol⁻¹. MRCI SO coupling constants |A| are 153 (a³Γ), 285 (b³Π), 351 (c³Δ), and 122 (d³Φ) cm⁻¹.

3. Higher States. Table 4 collects MRCI+Q results on 22 bound states, 11 singlets, 4 triplets, and 7 quintets, all correlating adiabatically to the ground-state atoms; see also Figure 3. Results on 4 more bound states of septet multiplicity are listed in Table 4 with their PECs displayed in Figure 3, correlating to the second channel Co⁺(a⁵F) + O(³P). Assuming that our deductions for the first 5 states of CoO⁺, concerning core + relativistic effects (vide supra), apply to the higher states as well, more reliable r_e and D_e estimates for the 22 states can be obtained by reducing uniformly all r_e by ~0.02 Å and by increasing D_e values by ~3.5 kcal/mol.

For all 27 states correlating to the first channel, a Co⁺ to O charge migration is observed ranging from ~0.1 (1¹Σ⁺) to ~0.5 e⁻ (1⁵Γ, 2⁵Δ), increasing monotonically from singlets to triplets

to quintets. For the 4 septets, as expected, interaction energies are much lower (~9 kcal/mol), certainly of a “van der Waals” nature, the bond distances being larger by ~0.7 Å than those of the lower spin states. No Co⁺ to O charge transfer is observed for the septets; see Table 4.

C. CoO⁻. The only experimental information on CoO⁻ is its ionization energy (or EA of CoO), IE = 1.45 ± 0.01 eV.^{11,17} Theoretical work is limited to DFT calculations (see the Introduction). A reliable experimental dissociation energy, however, can be obtained indirectly through energy conservation relation

$$\begin{aligned}
 D_0(\text{CoO}^-) &= D_0(\text{CoO}) + \text{EA}(\text{CoO}) - \text{EA}(\text{O}) \\
 &= (4.08 \pm 0.09)^{20} + (1.45 \pm 0.01)^{11,17} \\
 &\quad - (1.461)^{47} \text{ eV} \\
 &= 93.8 \pm 2.1 \text{ kcal mol}^{-1}
 \end{aligned}$$

very close to the D_0 value of the neutral species CoO. As a matter of fact, $D_0(\text{CoO}) = D_0(\text{CoO}^-)$, because the electron affinities of CoO and O happen to be equal. From the energy conservation relation it is clear that if EA(MO) < EA(O), then $D(\text{MO}^-) < D(\text{MO})$ and vice versa. Given that the EAs of the MO series (M = Sc–Ni) differ by about 0.15 eV, we can ascertain that $D(\text{MO}) \approx D(\text{MO}^-)$. In particular, EA = 1.35 (ScO), 1.30 (TiO), 1.30 (VO), 1.22 (CrO), 1.375 (MnO) eV (refs 1,2), 1.50 (FeO),³ 1.45 (CoO),^{11,17} and 1.46 (NiO) eV.⁴⁸ Therefore, for the first five MOs, $D(\text{MO}) = D(\text{MO}^-) + \delta$, with 2 (MnO) < δ < 5 (CrO) kcal/mol, while for the oxides FeO, CoO, and NiO, $D(\text{MO}) = D(\text{MO}^-)$ within 1 kcal/mol. With an EA = 1.777 eV,⁴⁹ the neutral CuO should have a binding energy smaller than its anion CuO⁻ by the difference $\delta = \text{EA}(\text{CuO}) - \text{EA}(\text{O}) = (1.777 - 1.461) \text{ eV} = 7.3 \text{ kcal/mol}$, which is indeed the case.⁴⁹

Table 4. MRCI+Q Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal mol⁻¹), Harmonic Frequencies and Anharmonicity Corrections ω_e , $\omega_e x_e$ (cm⁻¹), Rotational–vibrational Coupling Constants $\alpha_e \times 10^3$ (cm⁻¹), Mulliken Charges on Co q_{Co} , and Energy Separations T_e (cm⁻¹) of Higher States of Co¹⁶O⁺; in Parentheses, Theoretical Results from the Literature (footnote c), in Brackets Experimental Results

| state ^a | $-E$ | r_e | D_e^b | ω_e | $\omega_e x_e$ | α_e | q_{Co} | T_e |
|--|------------|------------------|----------------|--------------------------|----------------|------------|----------|---------------|
| 1 ³ Σ ⁻ (a ³ F) | 1456.48971 | 1.709 (1.717) | 43.0 (51.0) | 639 (671) | 5.7 | 1.6 | 1.39 | 9577 |
| 2 ³ Π (a ³ F) | 1456.48763 | 1.696 (1.714) | 41.6 (49.4) | 654 (647) | 1.9 | 5.0 | 1.35 | 10033 |
| 1 ³ Σ ⁺ (a ³ F) | 1456.48692 | 1.720 (1.728) | 41.3 (49.2) | 634 (671) | 0.9 | 3.3 | 1.39 | 10189 |
| 2 ³ Δ (a ³ F) | 1456.48336 | 1.744 (1.746) | 39.0 (47.5) | 624 (658) | 3.3 | 1.5 | 1.41 | 10970 |
| 1 ⁵ Π (a ³ F) | 1456.48203 | 1.771 (1.760) | 38.1 (47.6) | 680 (687) | 3.0 | 2.5 | 1.43 | 11263 |
| 1 ¹ Π (a ³ F) | 1456.47910 | 1.625 | 36.2 | 682(=ΔG _{1/2}) | | | 1.15 | 11906 |
| 1 ¹ Σ ⁺ (a ³ F) | 1456.47898 | 1.643 | 36.3 | 732(=ΔG _{1/2}) | | | 1.09 | 11933 |
| 1 ⁵ Σ ⁺ (a ³ F) | 1456.47696 | 1.790 (1.770) | 35.0 (45.2) | 647 (656) | 2.7 | 2.4 | 1.45 | 12376 |
| 1 ⁵ Γ (a ³ F) | 1456.47643 | 1.826 (1.818) | 34.6 (42.7) | 682 (687) | 3.0 | 2.7 | 1.47 | 12491 |
| 1 ¹ Δ (a ³ F) | 1456.47590 | 1.595 | 34.3 | 765 | 35.9 | 14.4 | 1.22 | 12609 |
| 2 ¹ Σ ⁺ (a ³ F) | 1456.47196 | 1.611 | 31.7 | 870 | 20.7 | 7.5 | 1.24 | 13473 |
| 1 ⁵ Φ (a ³ F) | 1456.47140 | 1.829 (1.819) | 31.5 (40.8) | 664 (668) | 2.8 | 2.6 | 1.42 | 13596 |
| [B ⁵ Φ _s] ^d | | [1.87 ± 0.01] | | [608] | | | | [16 713 ± 10] |
| 2 ⁵ Δ (a ³ F) | 1456.46833 | 1.841 (1.834) | 29.6 (38.0) | 659 (662) | 2.8 | 2.8 | 1.47 | 14269 |
| 2 ⁵ Π (a ³ F) | 1456.46823 | 1.838 (1.828) | 29.5 (38.7) | 657 (657) | 2.9 | 2.7 | 1.43 | 14291 |
| [C ⁵ Π ₃] ^d | | [1.86 ± 0.015] | | | | | | [17 588 ± 10] |
| 1 ¹ Φ (a ³ F) | 1456.46637 | 1.733 | 28.3 | 730 | 22.7 | 7.2 | 1.11 | 14699 |
| 1 ⁵ Σ ⁻ (a ³ F) | 1456.46571 | 1.847 (1.840) | 27.9 (36.6) | 650 (650) | 3.0 | 2.9 | 1.47 | 14844 |
| 2 ¹ Δ (a ³ F) | 1456.46375 | 1.660 | 26.7 | 709(=ΔG _{1/2}) | | | 1.19 | 15274 |
| 2 ¹ Π (a ³ F) | 1456.46239 | 1.685 | 25.8 | 682(=ΔG _{1/2}) | | | 1.28 | 15573 |
| 2 ¹ Φ (a ³ F) | 1456.45582 | 1.749 | 21.6 | 682(=ΔG _{1/2}) | | | 1.20 | 17016 |
| 1 ¹ Γ (a ³ F) | 1456.45505 | 1.652 | 21.2 | 725(=ΔG _{1/2}) | | | 1.23 | 17185 |
| 1 ¹ Σ ⁻ (a ³ F) | 1456.44462 | 1.689 | 14.7 | 466(=ΔG _{1/2}) | | | 1.25 | 19472 |
| 3 ¹ Π (a ³ F) | 1456.44040 | 1.750 | 12.2 | 700(=ΔG _{1/2}) | | | 1.14 | 20399 |
| 1 ⁷ Φ (a ⁵ F) | 1456.42115 | 2.291 | 10.6 | 215 | 3.5 | 4.8 | 0.92 | 24624 |
| 1 ⁷ Σ ⁺ (a ⁵ F) | 1456.42078 | 2.284 | 10.5 | 205 | 3.2 | 4.6 | 0.93 | 24706 |
| 1 ⁷ Π (a ⁵ F) | 1456.41791 | 2.403 | 8.7 | 187 | 3.5 | 4.9 | 0.94 | 25336 |
| 1 ⁷ Δ (a ⁵ F) | 1456.41488 | 2.578 | 6.7 | 164 | 3.3 | 4.8 | 0.96 | 26000 |

^aFor MRCI results see Table S4 of Supporting Information, ref 50. ^bWith respect to adiabatic products; in parentheses after the molecular term symbol are the end term symbol of Co⁺. ^cReference 30. ^dReference 27, rotational photodissociation spectroscopy.

The ground-state channel Co (a⁴F; 4s²3d⁷) + O⁻(²P) gives rise to 24 molecular states of CoO⁻, 12 triplets and 12 quintets (vide supra). We have calculated MRCI-L+Q/ASζ PECs for 7 states, namely, ⁵Δ, ³Φ, ³Σ⁻, ³Δ, ³Γ, ⁵Γ, and ⁵Σ⁻. Numerical results are listed in Table 5, while MRCI-L+Q/ASζ PECs are shown in Figure 4. For the ground state only (X⁵Δ), in addition to the MRCI-L approach, the ACPF-L and RCCSD(T) methods have been also applied.

With no doubt, the ground state of CoO⁻ is ⁵Δ followed by a ³Φ state about 2000 cm⁻¹ higher. Core subvalence effects seem to be of no importance, at least for the X-state at the coupled-cluster method. At the highest level of theory MRCI+L+DKH2+Q(ACPF-L+DKH2+Q) [C-RCCSD(T)+DKH2+Q], we obtain $r_e = 1.664$ (1.664) [1.650] Å and

$D_0(=D_e - \omega_e/2) = 84.3$ (86.1) [89.9] kcal/mol, the best value with respect to experiment being that of RCCSD(T). The dominant MRCI configuration, Mulliken populations, and the σ orbitals of the X⁵Δ state are

$$|X^5\Delta\rangle_{A_1} \approx 0.86|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^1 1\delta_-^1\rangle$$

$$4s^{1.96} 4p_z^{0.28} 4p_x^{0.07} 4p_y^{0.07} 3d_z^2 3d_{xz}^1 3d_{yz}^1 3d_{x^2-y^2}^{1.26} 3d_{xy}^{1.98} 3d_{xy}^{1.00}$$

$$/2s^{1.79} 2p_z^{1.41} 2p_x^{1.65} 2p_y^{1.65}$$

$$2\sigma \approx (0.56)4s - (0.49)2p_z,$$

$$3\sigma \approx (0.29)4s - (0.70)3d_{z^2} + (0.57)2p_z,$$

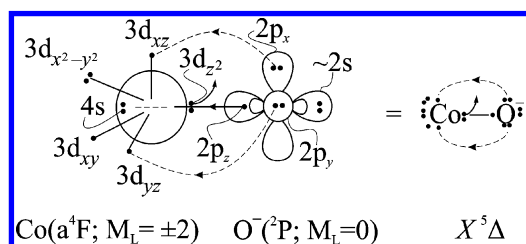
$$4\sigma \approx (0.53)4s + (0.70)3d_{z^2} + (0.52)2p_z$$

Table 5. Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal mol⁻¹), Harmonic Frequencies and Anharmonicity Corrections ω_e , $\omega_e x_e$ (cm⁻¹), Rotational–Vibrational Coupling Constants $\alpha_e \times 10^3$ (cm⁻¹), Mulliken Charges on Co q_{Co} , and Energy Separations T_e (cm⁻¹) of Co¹⁶O⁻

| method ^a | -E | r_e | D_e | ω_e | $\omega_e x_e$ | α_e | q_{Co} | T_e |
|---|------------|-------|-------|------------|----------------|------------|----------|-------|
| X⁵Δ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.84054 | 1.679 | 85.2 | 805 | 6.1 | 2.0 | -0.44 | 0.0 |
| MRCI-L+Q | 1456.88509 | 1.673 | 87.2 | 825 | 5.2 | 2.2 | | 0.0 |
| MRCI-L+DKH2 | 1467.33439 | 1.671 | 83.4 | 854 | 6.7 | 2.7 | | 0.0 |
| MRCI-L+DKH2+Q | 1467.37966 | 1.664 | 85.5 | 880 | 8.7 | 2.2 | | 0.0 |
| ACPF | 1456.89057 | 1.675 | 88.7 | 848 | 8.5 | 2.6 | | 0.0 |
| ACPF+DKH2 | 1467.38569 | 1.664 | 87.3 | 840 | 6.0 | 3.6 | | 0.0 |
| RCCSD(T) | 1456.90528 | 1.662 | 90.2 | 911 | 8.2 | 3.0 | | 0.0 |
| RCCSD(T)+DKH2 | 1467.40188 | 1.651 | 89.6 | 903 | 8.3 | 3.2 | | 0.0 |
| C-RCCSD(T) | 1457.38009 | 1.662 | 89.5 | 921 | 8.0 | 3.1 | | 0.0 |
| C-RCCSD(T)+DKH2 | 1467.88142 | 1.650 | 91.2 | 918 | 8.0 | 3.4 | | 0.0 |
| ³Φ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.83177 | 1.663 | 79.7 | 823 | 7.3 | 3.8 | -0.35 | 1925 |
| MRCI-L+Q | 1456.87563 | 1.658 | 81.1 | 850 | 7.8 | 3.6 | | 2077 |
| MRCI-L+DKH2 | 1467.32696 | 1.655 | 78.9 | 832 | 7.8 | 3.8 | | 1632 |
| MRCI-L+DKH2+Q | 1467.37140 | 1.650 | 80.4 | 854 | 6.9 | 3.5 | | 1812 |
| ³Σ⁻ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.82116 | 1.638 | 73.2 | 779 | 8.2 | 4.1 | -0.50 | 4254 |
| MRCI-L+Q | 1456.86885 | 1.625 | 77.1 | 827 | 8.0 | 3.6 | | 3563 |
| MRCI-L+DKH2 | 1467.31614 | 1.633 | 72.0 | 782 | 7.9 | 5.1 | | 4005 |
| MRCI-L+DKH2+Q | 1467.36423 | 1.619 | 75.8 | 835 | 8.4 | 4.1 | | 3386 |
| ³Δ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.80082 | 1.668 | 60.3 | 864 | 28.2 | -0.1 | -0.48 | 8716 |
| MRCI-L+Q | 1456.84649 | 1.651 | 63.0 | 926 | 19.0 | -4.8 | | 8472 |
| MRCI-L+DKH2 | 1467.29789 | 1.659 | 60.5 | 840 | 27.0 | -3.3 | | 8011 |
| MRCI-L+DKH2+Q | 1467.34428 | 1.647 | 63.3 | 946 | 33.2 | -3.0 | | 7765 |
| ³Γ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.79632 | 1.846 | 57.5 | 467 | 2.0 | 3.4 | -0.60 | 9705 |
| MRCI-L+Q | 1456.83659 | 1.823 | 56.7 | 470 | 2.0 | 3.6 | | 10643 |
| MRCI-L+DKH2 | 1467.29108 | 1.837 | 56.3 | 457 | 1.2 | 3.4 | | 9505 |
| MRCI-L+DKH2+Q | 1467.33200 | 1.810 | 55.6 | 459 | 0.9 | 3.8 | | 10460 |
| ⁵Γ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.78630 | 1.982 | 51.2 | 486 | 4.5 | 4.0 | -0.44 | 11905 |
| MRCI-L+Q | 1456.82506 | 1.974 | 49.6 | 489 | 3.8 | 3.9 | | 13174 |
| MRCI-L+DKH2 | 1467.28053 | 1.982 | 49.6 | 481 | 4.6 | 4.1 | | 11820 |
| MRCI-L+DKH2+Q | 1467.31982 | 1.974 | 48.0 | 484 | 4.2 | 4.0 | | 13134 |
| ⁵Σ⁻ (a⁴F) | | | | | | | | |
| MRCI-L | 1456.77677 | 2.006 | 45.4 | 429 | 12.7 | -0.1 | -0.43 | 13996 |
| MRCI-L+Q | 1456.81532 | 2.000 | 43.7 | 410 | 17.6 | -2.5 | | 15312 |
| MRCI-L+DKH2 | 1467.27119 | 2.006 | 43.8 | 427 | 18.9 | -0.8 | | 13871 |
| MRCI-L+DKH2+Q | 1467.31028 | 2.000 | 42.0 | 404 | 26.5 | -4.6 | | 15228 |

^aSee Table 1 for explanation of acronyms and symbols.

The vbL diagram below gives a fair visualization of the Co + O⁻ interaction in the X⁵Δ state.



The bonding comprises a 2-center–5e⁻ σ and two 2-center–3e⁻ π interactions. About 0.7 e⁻ are moving from O⁻ to Co through the π frame, while ~0.2 e⁻ are transferred back through the σ frame, resulting in a net O⁻ to Co charge migration of ~0.5 e⁻.

The vbL diagram above is very similar to the diagram of the X⁴Δ state of the neutral species after attaching one electron to the σ-frame of the latter.

For the six higher states of symmetries, ³Φ, ³Σ⁻, ³Δ, ³Γ, ⁵Γ, and ⁵Σ⁻ numerical results at the MRCI-L approach are collected in Table 5. All six states are relatively strongly bound with respect to the ground-state channel Co(a⁴F) + O⁻(²P), with bond distances ranging from 1.62 (³Σ⁻) to 2.00 Å (⁵Σ⁻). Four of the states, namely, X⁵Δ, a³Φ, b³Σ⁻ and ³Δ, are stable with respect to the X⁴Δ state of CoO at the MRCI-L+Q and MRCI-L+DKH2+Q/ASζ levels of theory. To be more specific, the total energy of the ³Δ state of CoO⁻ is lower by about 5 mE_h than the X⁴Δ state of CoO; see Tables 1 and 5. The rest of the states, ³Γ, ⁵Γ, and ⁵Σ⁻, are certainly unstable with respect to the X⁴Δ state of CoO by ~4, 16, and 26 mE_h, respectively. A considerable O⁻ to Co

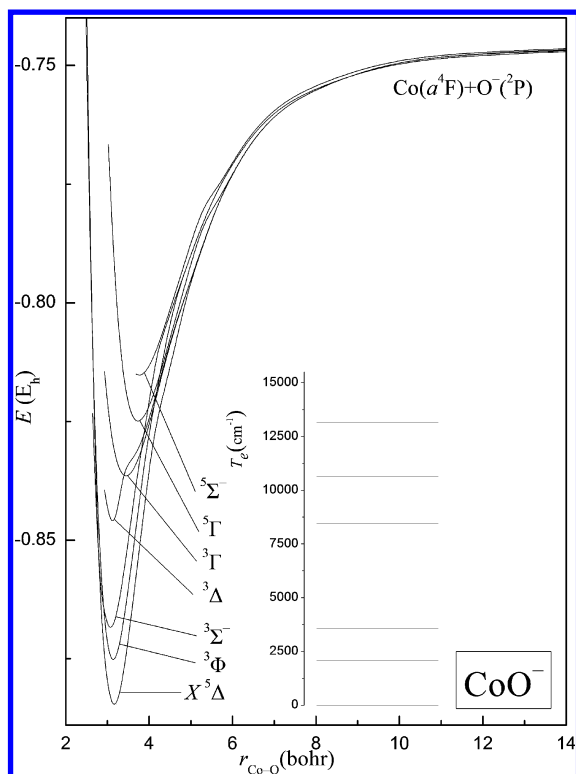


Figure 4. MRCI-L+Q/A5 ζ adiabatic PECs and energy level diagram (inset) of 7 bound states of CoO⁻. The ordering follows that of Table 5. All energies are shifted by +1456 E_h.

charge transfer of about 0.5 e⁻ is observed, whereas all six states are of intense multireference character; see Tables S7 and S8 in the Supporting Information.⁵⁰ The MRCI SO coupling constants of X⁵Δ and ³Φ states are $A = 139$ and 254 cm⁻¹, respectively.

IV. SUMMARY AND REMARKS

The present work is a comprehensive high-level ab initio study of the CoO and its ions, CoO⁺ and CoO⁻, related to our recently published work in the 3d MO^{0±} (M = Sc–Fe) series.^{1–3} Previous ab initio studies on CoO and CoO⁺ have been very limited indeed, being completely absent for CoO⁻; similarly, experimental results on the latter are practically nonexistent. The intricate electronic structure and high-density spectrum of the MO^{0±} species dictate a multireference method of calculation and this is our method of choice in the present work. Using the MRCI method combined with augmented correlation consistent basis sets of quintuple quality (MRCI (+Q)/A5 ζ), we have constructed full PECs for 50, 31, and 7 bound states of CoO, CoO⁺, and CoO⁻, respectively. It should be mentioned, however, that as the number of valence electrons increases along the MO series (M = Sc–Ni), the efficiency of the MRCI method decreases; see, for instance, refs 1–3. The situation becomes more involved when one is trying to correct for subvalence (3s²3p⁶) core correlation and/or scalar relativistic effects (DKH). In the first case, size nonextensivity effects increase steeply, whereas in the second DKH corrections can create serious imbalances. In an effort to secure more credible results, for the first 5 states of CoO and CoO⁺ and the X⁵Δ state of CoO⁻ we have performed multireference ACPF and single-reference RCCSD(T) calculations correcting as well for core and scalar relativistic effects. In addition, for these five states of

CoO and CoO⁺, and all 7 states of CoO⁻, larger MRCI calculations have been done (MRCI-L) by increasing the size of the reference space(s).

We report energetics, common spectroscopic constants, dipole moments (CoO), Mulliken charges, and spin–orbit coupling constants (A) for the first few low-lying states of CoO, CoO⁺, and CoO⁻. Our conclusions are summarized below.

1. It has been confirmed that the ground states of CoO and CoO⁺ are of ⁴Δ and ⁵Δ symmetries, respectively, whereas the ground state of CoO⁻, established with certainty for the first time, is ⁵Δ.
2. Considering the very complex electronic structure of these molecules, our results are in fair to good agreement with experiment. An interesting discrepancy between theory and experiment, however, is observed in the ordering of the first excited states of CoO. While experimentally the first excited state is ⁴Σ⁻ at $T = 3390$ cm⁻¹, our calculations indicate instead a ⁶Δ state at ~ 4400 cm⁻¹, locating the ⁴Σ⁻ state at ~ 5100 cm⁻¹ or some 700 cm⁻¹ above the ⁶Δ state. In addition, a ⁴Φ state, calculated to be just 500 cm⁻¹ above the ⁶Δ, has never been observed experimentally. Finally, the ⁶Δ state is located experimentally at $T = 7028$ cm⁻¹, about 2600 cm⁻¹ higher than the calculated one.
3. The neutral molecule CoO is fairly ionic with a Co to O Mulliken charge transfer ranging from less than 0.50 (¹Π) to 0.80 (²Σ⁻). Even in the cation Co⁺–O a considerable Co⁺ to O Mulliken charge transfer is found, ranging from 0.1 (¹Σ⁺) to 0.5 (¹Σ⁺, ²Σ^Δ) electrons. On the other hand, in the anion CoO⁻ the negative charge is almost equally distributed between the two atoms for all 7 states examined, i.e., a flow of ~ 0.5 e⁻ is observed from O⁻ to Co.
4. To our knowledge, there is no experimental dipole moment for the ground or any other state of CoO. For the X⁴Δ state of CoO the finite field calculated dipole moment ranges, in all methods employed, from 4.3 to 4.6 D; the recommended value is $\mu_{\text{FF}} = 4.5 \pm 0.1$ D. Electric dipole moments (μ_{FF}) are, in general, large, varying at the MRCI+Q level between 1.8 (^aΔ) and 5.0 (^BΣ⁻, ^AΦ, ^CΠ) D, most of them clustering around 3 D.
5. Results obtained at the MRCI+Q level do not differ significantly from all other approaches including core and relativistic effects. Therefore, all our results obtained at the MRCI+Q level can be considered better than of semiquantitative nature due to cancellation of errors. This is corroborated, for instance, by contrasting experimental versus MRCI+Q separation energies (T_e) for higher states of CoO (theoretical values in parentheses): $T_e = 10131 \pm 5$ (11 068), 13 950.07 (13 031), 15 884.64 (14 815), 15 650.679 (15 932), and 21 046 (19 418) cm⁻¹ for the ¹Δ, ³Δ, ⁴Π, ⁴Δ, and ³Φ states, respectively.
6. An effort has been made to adumbrate the bonding characteristics for a few lower states of CoO and the X-states of CoO⁺ and CoO⁻. It should be stated, however, that the bonding is quite complicated due to the multireference nature of these systems and their interaction with ionic channels. Thus, conventional bonding interpretations based on a naïve orbital picture are not realistic and can lead to wrong conclusions.

It is our belief that the present study of CoO and CoO[±] is a significant contribution to the literature of the 3d transition metal monoxides. In particular, the construction for the first time of a

very large number of full potential energy curves along with corresponding calculated spectroscopic parameters can provide valuable information to the understanding of their complex spectra and other properties. From the theoretical point of view, it is indeed remarkable that a huge effort is required for obtaining useful results, even for rather light diatomic molecules of a certain type like the ones examined here, when employing all-electron ab initio wave function methods.

■ ASSOCIATED CONTENT

■ Supporting Information

MRCI results for higher states of CoO and CoO⁺ as well as leading MRCI/AS ζ configurations, Mulliken atomic populations, and atomic charges for all species, CoO^{0±}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Miliordos, E.; Mavridis, A. *J. Phys. Chem. A* **2007**, *111*, 1953.
- (2) Miliordos, E.; Mavridis, A. *J. Phys. Chem. A* **2010**, *114*, 8536.
- (3) Sakellaris, C. N.; Miliordos, E.; Mavridis, A. *J. Chem. Phys.* **2011**, *134*, 234308.
- (4) Merer, A. *J. Annu. Rev. Phys. Chem.* **1989**, *40*, 407.
- (5) Harrison, J. F. *Chem. Rev.* **2000**, *100*, 679 and references therein.
- (6) Gong, Y.; Zhou, M.; Andrews, L. *Chem. Rev.* **2009**, *109*, 6765.
- (7) Rosen, B. *Nature* **1945**, *156*, 570.
- (8) Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1966**, *45*, 4158.
- (9) DeVore, T. C.; Gallaher, T. N. *J. Chem. Phys.* **1979**, *71*, 474.
- (10) Green, D. W.; Reedy, G. T.; Kay, J. G. *J. Mol. Spectrosc.* **1979**, *78*, 257.
- (11) Adam, A. G.; Azuma, Y.; Barry, J. A.; Huang, G.; Lyne, M. P. J.; Merer, A. J.; Schröder, J. O. *J. Chem. Phys.* **1987**, *86*, 5231.
- (12) Fisher, E. R.; Elkind, J. L.; Clemmer, D. E.; Georgiadis, R.; Loh, S. K.; Aristov, N.; Sunderlin, L. S.; Armentrout, P. B. *J. Chem. Phys.* **1990**, *93*, 2676.
- (13) Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 1674.
- (14) Ram, R. S.; Jarman, C. N.; Bernath, P. F. *J. Mol. Spectrosc.* **1993**, *160*, 574.
- (15) Clouthier, D. J.; Huang, G.; Merer, A. J.; Friedman-Hill, E. J. *J. Chem. Phys.* **1993**, *99*, 6336.
- (16) Barnes, M.; Clouthier, D. J.; Hajigeorgiou, P. G.; Huang, G.; Kingston, C. T.; Merer, A. J.; Metha, G. F.; Peers, J. R. D.; Rixon, S. J. *J. Mol. Spectrosc.* **1997**, *186*, 374.
- (17) Li, X.; Wang, L.-S. *J. Chem. Phys.* **1999**, *111*, 8389.
- (18) Namiki, K. C.; Saito, S. *J. Chem. Phys.* **2001**, *114*, 9390.
- (19) Danset, D.; Manceron, L. *J. Phys. Chem. A* **2003**, *107*, 11324.
- (20) Liu, F.; Li, F.-X.; Armentrout, P. B. *J. Chem. Phys.* **2005**, *123*, 064304.
- (21) McLamarras, S. K.; Sheridan, P. M.; Ziurys, L. M. *Chem. Phys. Lett.* **2005**, *414*, 301.
- (22) Guo, J.; Wang, T.; Zhang, Z.; Chen, C.; Chen, Y. *J. Mol. Spectrosc.* **2006**, *240*, 45.
- (23) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 2123.
- (24) Bauschlicher, C. W., Jr.; Maitre, P. *Theor. Chim. Acta* **1995**, *90*, 189.
- (25) Baranowska, A.; Siedlecka, M.; Sadlej, A. J. *Theor. Chem. Acc.* **2007**, *118*, 959.
- (26) (a) Piechota, J.; Suffczyński, M. *Phys. Rev. A: At. Mol. Opt. Phys.* **1993**, *48*, 2679. (b) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **2000**, *104*, 5374. (c) Bridgeman, A. J.; Rothery, J. *J. Chem. Soc., Dalton Trans.* **2000**, 211. (d) Uzunova, E. L.; Nikolov, G.; St.; Mikosch, H. *J. Phys. Chem. A* **2002**, *106*, 4104. (e) Gutsev, G. L.; Andrews, L.; Bauschlicher, C. W., Jr. *Theor. Chem. Acc.* **2003**, *109*, 298. (f) Dai, B.; Deng, K.; Yang, J.; Zhu, Q. *J. Chem. Phys.* **2003**, *118*, 9608. (g) Uzunova, E. L.; Nikolov, G. St.; Mikosch, H. *ChemPhysChem* **2004**, *5*, 192. (h) Jensen, K. P.; Roos, B. O.; Ryde, U. *J. Chem. Phys.* **2007**, *126*, 014103. (i) Uzunova, E. L.; Mikosch, H.; Nikolov, G. St. *J. Chem. Phys.* **2008**, *128*, 094307. (j) Liu, L.; Zhao, R.-N.; Han, J.-G.; Liu, F.-Y.; Pan, G.-Q.; Sheng, L.-S. *J. Phys. Chem. A* **2009**, *113*, 360.
- (27) Kamariotis, A.; Hayes, T.; Bellert, D.; Brucat, P. J. *Chem. Phys. Lett.* **2000**, *316*, 60.
- (28) Carter, E. A.; Goddard, W., III. *J. Phys. Chem.* **1988**, *92*, 2109.
- (29) Sodupe, M.; Branchadell, V.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Phys. Chem.* **1997**, *101*, 7854.
- (30) Nakao, Y.; Hirao, K.; Taketsugu, T. *J. Chem. Phys.* **2001**, *114*, 5216.
- (31) Fiedler, A.; Schröder, D.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 10734.
- (32) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107.
- (33) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (34) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (35) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718. Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219; *ibid* **2000**, *112*, 3106E.
- (36) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803. Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.
- (37) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.
- (38) Hess, B. A. *Phys. Rev. A: At. Mol. Opt. Phys.* **1985**, *32*, 756; *ibid.* **1986**, *33*, 3742.
- (39) Jansen, H. B.; Ross, P. *Chem. Phys. Lett.* **1969**, *3*, 140. Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (40) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61. Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *52*, 403.
- (41) Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413. Werner, H.-J.; Knowles, P. J. *Theor. Chim. Acta* **1990**, *78*, 175.
- (42) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. MOLPRO, version 2006.1, a package of ab initio programs; see <http://www.molpro.net>.
- (43) Ralchenko, Yu.; Kramida, A. E.; Reader, J. NIST ASD Team (2010). NIST Atomic Spectra Database (version 4.0), [Online]. Available at: <http://physics.nist.gov/asd>. National Institute of Standards and Technology: Gaithersburg, MD.
- (44) Bunge, C. E.; Barrientos, J. A.; Bunge, A. V. *At. Data Nucl. Data Tables* **1993**, *53*, 113.
- (45) Tzeli, D.; Mavridis, A. *J. Chem. Phys.* **2003**, *118*, 4984; *ibid.* **2010**, *132*, 194312.
- (46) Herschbach, D. R.; Laurie, W. V. *J. Chem. Phys.* **1961**, *35*, 458.
- (47) Blondel, O.; Chaibi, W.; Delsart, C.; Drag, C.; Goldfarb, F.; Kröger, S. *Eur. Phys. J. D* **2005**, *33*, 335.
- (48) Ramond, T. M.; Davico, G. E.; Hellberg, F.; Svedberg, F.; Salén, P.; Söderqvist, P.; Lineberger, W. C. *J. Mol. Spectrosc.* **2002**, *216*, 1.

(49) Polak, M. L.; Gilles, M. K.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 3460.

(50) See Supporting Information for MRCI results for higher states of CoO and CoO⁺ as well as leading MRCI/AS ζ configurations, Mulliken atomic populations, and atomic charges for all species, CoO^{0 \pm} .