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Potential energy curves for neutral and multiply charged carbon monoxide

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Abstract. Potential energy curves of various electronic states of CO^{n+} ($0 \leq n \leq 6$) are generated at MRCI/CASSCF level using cc-pvQZ basis set and the results are compared with available experimental and theoretical data.

Keywords. Potential energy curves; *ab initio* calculations; multiply charged; excited states; multireference configuration interaction.

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1. Introduction

Carbon monoxide (CO) is an important diatomic species, and is the second-most abundant molecule in interstellar space. Therefore, it has been the subject of a lot of theoretical and experimental investigations [1–6]. A complete understanding of the properties of CO would be incomplete without understanding the properties of multiply charged CO species. Due to recent advances in experimental techniques, researchers are able to generate CO^{n+} ions up to $n = 9$ [7,8]. However, so many facts on the system remain unexplained due to the lack of accurate potential energy curves (PECs) of multiply charged CO. Experimental and theoretical results available on multiply charged ions have been reviewed elsewhere [9,10]. Although both mono and dications of CO have been investigated extensively [11–18], very few theoretical results are available on trication [19,20]. To the best of our knowledge, there is only one unrestricted Hartree–Fock and MP2 calculation reported for higher charged CO [8]. Therefore, a comprehensive study of CO^{n+} ions ($n \leq 6$) has been undertaken using the multireference configuration interaction (MRCI) method with complete active space self-consistent field (CASSCF) reference wave function.

Section 2 presents the methodology employed, while §3 describes the results and discussion. In §4, summary and conclusions are given.

2. Methodology

Ab initio calculations have been carried out at MRCI/CASSCF level with Dunning cc-pVQZ basis set using MOLPRO suite of programs [22]. MOLPRO uses Abelian subgroup of the actual point group of a molecule. In the case of CO it has taken C_{2v} as a point group, in which the two core orbitals correspond to A_1 symmetry. Out of the eight valence orbitals, four are of A_1 symmetry, two are of B_1 symmetry and two are of B_2 symmetry. For the excited states of CO^+ corresponding to $^2\Pi$ symmetry, CO^{2+} corresponding to $^1\Sigma^+$ and $^3\Pi$ states and CO^{3+} corresponding to $^2\Pi$ symmetry, three valence orbitals of A_1 symmetry, two valence orbitals of B_1 symmetry and two valence orbitals of B_2 symmetry were chosen as the active space for the CASSCF calculation. For all other calculations, full valence and one additional orbital of A_1 symmetry were chosen as the active space, which yields reference wave function for subsequent MRCI calculations.

3. Results and discussion

The potential energy curve (PEC) for CO as obtained from our calculations for its ground electronic state $^1\Sigma^+$, with the electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$ is plotted in figure 1a. The zero energy corresponds to the minimum of the curve, which occurs at the equilibrium bond distance $r_\mathrm{e} = 1.131$ Å. The depth of the potential well is found to be 11.3 eV. Vibrational frequency calculations yield $\omega_\mathrm{e} = 2167$ cm^{-1} and the zero point energy (ZPE) = 0.13 eV, within the harmonic oscillator approximation. These results are in excellent agreement with the experimental results of 1.128 Å and 11.21 eV, respectively (spectroscopic dissociation energy (D_0) = 11.09 eV, ZPE = 0.12 eV and $\omega_\mathrm{e} = 2169.8$ cm^{-1}) [3].

The PECs for CO^+ in its $^2\Sigma^+$ and $^2\Pi$ states corresponding to the configurations $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4$ and $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3$ are also plotted in figure 1a. Earlier calculations by Lavendy *et al*, done at MCSCF-CI level were restricted to the range 0.8–2.1 Å [18]. Martin and Feher had reported the results at the CASSCF level, over a wider range of bond distances [16]. In the present paper the PECs are generated for r in the range 0.8–5.9 Å. The minima in the PECs for $^2\Sigma^+$ and $^2\Pi$ states occur at 1.118 Å and 1.249 Å, respectively, and are in excellent agreement with the experimental values 1.115 and 1.243 Å [3]. The value of D_0 for the $^2\Sigma^+$ state is found to be 8.31 eV (ω_e = 2208 cm^{-1} and ZPE = 0.136 eV), which is in excellent agreement with the experimental value 8.33 eV [3]. For the $^2\Pi$ state, $D_0 = 5.81$ eV ($\omega_\mathrm{e} = 1547$ cm^{-1}, ZPE = 0.09 eV). A close examination of the PEC for CO^+ reveals that the vertical ionization potential (I_1) for CO is 13.78 and 16.32 eV corresponding to the formation of CO^+ in its $^2\Sigma^+$ and $^2\Pi$ states, respectively (table 1). The reported experimental value of $I_1 = 14.01$ eV clearly indicates the formation of CO^+ ($^2\Sigma^+$) under laboratory conditions [3].

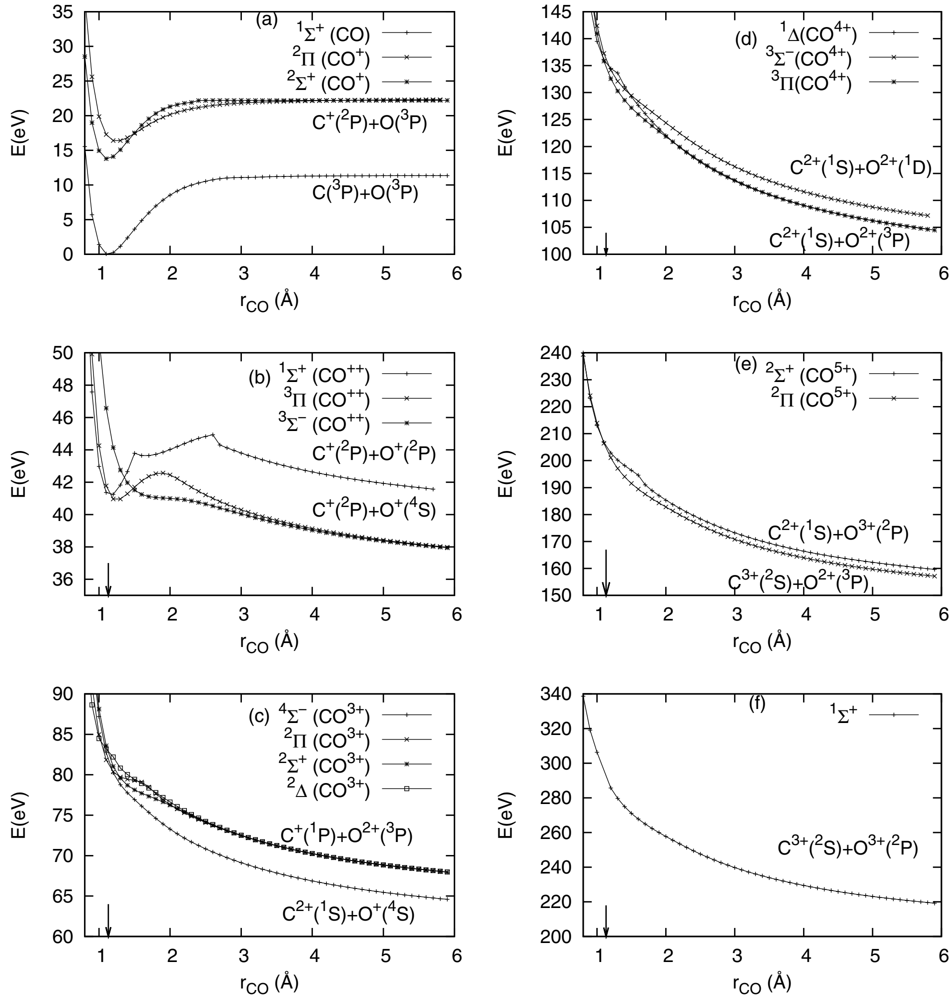

Figure 1. PECs for CO^{n+} (n = 0–6) as obtained from MRCI/CASSCF calculations. The arrow along the x-axis in panels b–f shows the value of r_e for the ground state of neutral CO.

The PECs for CO^{2+} corresponding to $^1\Sigma^+$, $^3\Sigma^-$ and $^3\Pi$ states are plotted in figure 1b. The correct identification of the lowest-lying metastable electronic state of CO^{2+} has been the subject of discussion in the literature [8]. Near the Frank–Condon region (excitation from neutral CO) $^1\Sigma^+$ and $^3\Pi$ states are nearly degenerate. Present calculations reveal that $^3\Pi$ state is slightly lower in energy than the $^1\Sigma^+$ electronic state. The close-lying $^3\Sigma^-$ is a repulsive state. Hence it is expected to play an important role in the dissociation process. These observations are in accord with the earlier reported results [12,13]. The equilibrium bond lengths for $^1\Sigma^+$ and $^3\Pi$ state are found to be 1.159 and 1.247 Å, respectively. The corresponding ω_e values are 1923 and 1444 cm^{-1}, respectively. Earlier theoretical calculation at

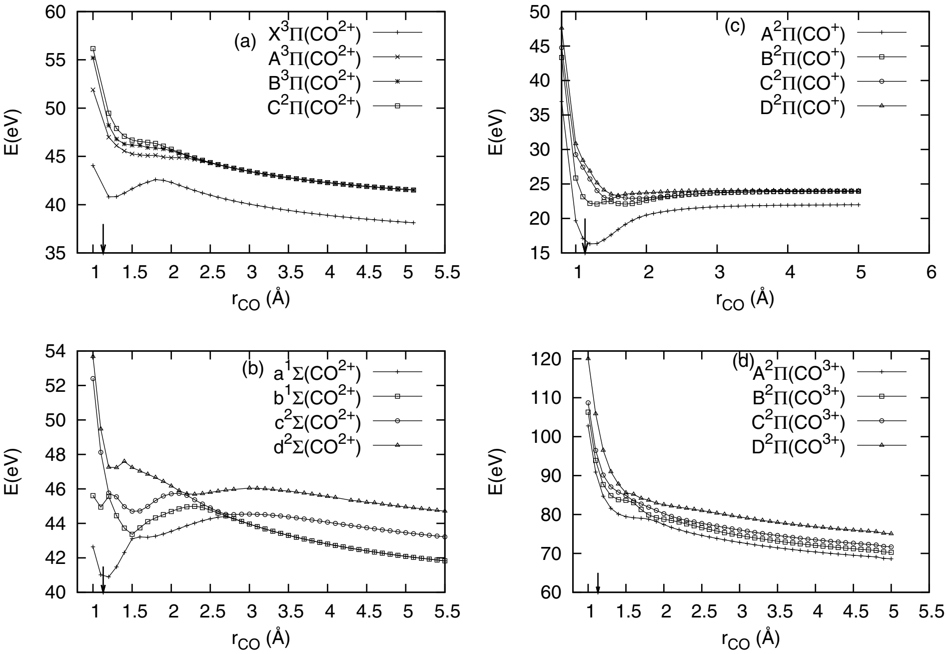

Figure 2. PECs for some of the excited states of CO^+, CO^{2+}, CO^{3+} as obtained from MRCI/CASSCF calculations. The arrow along the x-axis in panels (a–d) shows the value of r_e for the ground state of neutral CO.

MRCI level with a different basis set than ours for $^1\Sigma^+$ and $^3\Pi$ states have yielded $r_e = 1.226$ and 1.138 Å, respectively; $\omega_e = 1920$ and 1435 cm^{-1}, respectively [13]. The values of vertical ionization energy (I_2) for the $^1\Sigma^+$ and $^3\Pi$ electronic states are 41.11 and 41.39 eV, respectively. The corresponding experimental values are 41.700 and 41.294 eV, respectively [11,18]. The excited states of CO^{2+} of $^3\Pi$ symmetry shown in figure 2a are well separated from the ground $^3\Pi$ state and they do not show any indication of an avoiding crossing. Therefore, the barrier seen in the PEC for the $^3\Pi$ ground state of CO^{2+} must be due to a delicate balance between the Coulombic repulsion and covalent interaction. A close examination of the $^1\Sigma^+$ excited states of CO^{2+} plotted in figure 2b shows clearly that the barrier in the $^1\Sigma^+$ state is due to avoided crossing.

The potential energy curves of $^4\Sigma^+$, $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ states for CO^{3+} are plotted in figure 1c. Clearly there are two channels for CO^{3+} dissociation, one corresponding to $C^{2+}(^1S) + O^+(^4S)$ (channel 1) and the other one corresponding to $C^{2+}(^1S) + O^+(^2D)$ (channel 2). The former channel corresponds to $^4\Sigma^+$ state, which is purely repulsive. Its repulsive nature can be explained on the basis of weak interaction between the closed shell species $C^{2+}(1s^2 2s^2)$ and O^+ in its $1s^2 2s^2 2p^3$ configuration. It is understandable that there is very little covalent interaction between the two and that Coulombic repulsion is more dominant. The values of vertical ionization energy (I_3) for $^4\Sigma^+$, $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ states are found to be 81.82,

Table 1. Theoretically calculated vertical ionization energies (excitation from neutral CO, $r_e = 1.128$ Å) and kinetic energy release data for CO^{n+} ($0 \leq n \leq 6$) in various electronic states. Values in parentheses are from experiment.

Species	Electronic state	Vertical ionization energy (eV)[a]	Dissociation limit energy (eV)[a]	Kinetic energy release (eV)
CO	$^1\Sigma^+$		$C(^3P) + O(^3P)$	
CO^+	$^2\Sigma^+$	13.78 (14.1)[a]	$C^+(^2P) + O(^3P)$	
	$^2\Pi$	16.32	$C^+(^2P) + O(^3P)$	
CO^{2+}	$^1\Sigma^+$	41.11 (41.69)[b]	$C^+(^2P) + O^+(^2P)$	
	$^3\Sigma^-$	45.66	$C^+(^2P) + O^+(^4S)$	
	$^3\Pi$	41.39 (41.29)[c]	$C^+(^2P) + O^+(^4S)$	
CO^{3+}	$^4\Sigma^-$	81.82	$C^{2+}(^1S) + O^+(^4S)$	22.05 (22.72)[e]
	$^2\Sigma^+$	82.63	$C^{2+}(^1S) + O^+(^2D)$	15.95 (20.26)[e]
	$^2\Pi$	81.26	$C^{2+}(^1S) + O^+(^2D)$	15.40
	$^2\Delta$	83.13 (83.4)[d]	$C^{2+}(^1S) + O^+(^2D)$	17.27 (21.25)[e]
CO^{4+}	$^3\Sigma^-$	134.67	$C^{2+}(^1S) + O^{2+}(^3P)$	40.31
	$^3\Pi$	135.44	$C^{2+}(^1S) + O^{2+}(^3P)$	41.08 (41.07)[f]
	$^1\Delta$	136.27	$C^{2+}(^1S) + O^{2+}(^1D)$	39.01 (47.36)[f]
CO^{5+}	$^2\Sigma^+$	205.42	$C^{3+}(^2S) + O^{2+}(^1S)$	60.94
	$^2\Pi$	204.60	$C^{3+}(^2S) + O^{2+}(^3P)$	62.66 (67.62)[f]
CO^{6+}	$^1\Sigma^+$	290.97	$C^{3+}(^2S) + O^{3+}(^2P)$	94.25 (95.99)[f]
	$^3\Pi$	289.26	$C^{3+}(^2S) + O^{3+}(^2P)$	92.55 (97.62)[f]

[a]Ref. [3]; [b]ref. [11]; [c]ref. [19]; [d]refs [23–25]; [e]ref. [23] and [f]ref. [9].

82.63, 81.26 and 83.13 eV, respectively. The experimental value of 83.4 eV obtained from Auger spectra indicates the formation of the $^2\Delta$ state under laboratory conditions [23,24].

Potential energy curves for CO^{4+} in $^3\Sigma^-$, $^3\Pi$ and $^1\Delta$ states are illustrated in figure 1d. Here again there are two dissociative channels, one corresponding to $C^{2+}(^1S) + O^{2+}(^3P)$ and the other corresponding to $C^{2+}(^1S) + O^{2+}(^1D)$. From energy considerations it becomes clear that the first channel corresponds to the triplet electronic states while the second corresponds to the singlet electronic state. The value of vertical ionization potential (I_4) for $^3\Sigma^+$, $^3\Pi$ and $^1\Delta$ states are 134.67, 135.44 and 136.27 eV, respectively. Unfortunately, there are no experimental results available for CO^{4+}.

The PECs for the $^2\Pi$ and $^2\Sigma^+$ electronic states of CO^{5+} are plotted in figure 1e. The $^2\Pi$ state asymptotically corresponds to the $C^{3+}(^2S) + O^{2+}(^3P)$ channel and the $^2\Sigma^+$ state corresponds to the $C^{3+}(^2S) + O^{2+}(^1S)$ channel. The value of vertical ionization energy (I_5) for the $^2\Pi$ state is 204.6 eV and for the $^2\Sigma^+$ state is 205.4 eV. In figure 1f the PECs for the $^1\Sigma^+$ and $^3\Pi$ electronic states of CO^{6+} molecule are plotted.

Asymptotically they correspond to the $C^{3+}(^2S) + O^{3+}(^2P)$ channel. Vertical ionization energies are 290.97 and 289.26 eV for $^1\Sigma^+$ and $^3\Pi$ states, respectively.

The excited state PECs of CO^+ in the $^2\Pi$ state are plotted in figure 2c. It is evident that the ground state PEC is well-separated from the excited state potential energy curves. The PECs for the excited states of $^2\Pi$ symmetry for CO^{3+} are plotted in figure 2d. It is clear that there are several closely lying excited states of the same symmetry, resulting in several avoided crossings, which can result in metastable CO^{3+}.

4. Summary

Accurate potential energy curves for $CO(^1\Sigma^+)$, $CO^+(^2\Sigma^+, ^2\Pi)$, $CO^{2+}(^1\Sigma^+, ^3\Sigma^-, ^3\Pi)$, $CO^{3+}(^4\Sigma^+, ^2\Sigma^+, ^2\Pi, ^2\Delta)$, $CO^{4+}(^3\Sigma^+, ^3\Pi, ^1\Delta)$, $CO^{5+}(^2\Pi, ^2\Sigma^+)$ and $CO^{6+}(^1\Sigma^+, ^3\Pi)$ have been generated at MRCI/CASSCF level. In addition, the PECs of the excited electronic states of $CO^+(^2\Pi)$, $CO^{2+}(^1\Sigma^+,^3\Pi)$, $CO^{3+}(^2\Pi)$ are also generated. It is shown that the metastable state of $CO^{2+}(^1\Sigma^+)$ arises from avoided crossing, while the origin of the hump in the PEC for the $^3\Pi$ state could be due to a delicate balance between Coulombic and covalent interactions. Shallow minima found in the PECs for the $CO^{3+}(^2\Sigma^+, ^2\Pi, ^2\Delta)$ states arise from several avoided crossings.

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