Potential energy surfaces of NbCO

Hang Tan a, Muzhen Liao a, Dingguo Dai b, K. Balasubramanian b, *

a Center for Advanced Study and Department of Chemistry, Tsinghua University, Beijing 100084, PR China
b Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

Received 9 July 1998; in final form 5 October 1998

Abstract

Potential energy surfaces for the low-lying electronic states of the linear niobium carbon monoxide (NbCO) complex have been studied using the complete active space multi-configuration self-consistent field (CAS-MCSCF) followed by multi-reference singles + doubles configuration interaction (MRSDCI). The $^6\Sigma^+$ electronic state was found to be the ground state of Nb−CO, with a binding energy of 1.11 eV at the highest level of theory. The nature of bonding is discussed in terms of the wave function composition and the Mulliken populations. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of carbon monoxide (CO) on transition metal clusters, surfaces and atoms, as well as the properties of related transition metal clusters as a function of their sizes have been the topic of many experimental and theoretical studies [1–20]. The study of cluster–molecular interaction could provide significant insight into the nature of surface–molecular interactions that take place during chemisorption. Although a transition metal surface may contain many atoms, the interaction of a surface with a molecule like CO is often of local nature involving a few atoms. Previous theoretical studies [17–20] have shown that the atop chemisorption on a metal surface can be modeled with a single metal atom + CO, bridged chemisorption can be modeled using metal dimer + CO, three-fold chemisorption of metal (111) surfaces can be modeled using metal trimer + CO model and so on.

Chemisorption of carbon monoxide on transition metal surfaces is an important topic as transition metals play an important role in heterogeneous catalysis, and because of a fundamental desire to understand the nature of the bonding between various transition metals and ligands such as CO. The structure of CO adsorbed on a metallic surface is probed through infrared spectroscopy, among other techniques. While there are several experimental studies on the interaction of CO on transition metal surfaces, some recent studies have been focused on the interaction of CO on bimetallic surfaces that comprise either clean Nb or niobium oxide surfaces on which other transition metals such as Pd and Rh have been deposited [8–10,12,13]. As demonstrated by Somorjai and co-workers [12], niobium oxide influences the reactivity of transition metals such as palladium and rhodium in the hydrogenation reaction of CO. For

* Corresponding author. E-mail: kbalu@asu.edu

0009-2614/98/$ - see front matter © 1998 Elsevier Science B.V. All rights reserved.
PII: S0009-2614(98)01145-2
example, Jirsak et al. [8] have studied thermally programmed desorption of CO on thin and thick palladium overlayers deposited onto clean and oxidized niobium surfaces.

Beutel et al. [10] have reported the FTIR spectra of CO chemisorbed on Nb-oxide-promoted Rh/SiO$_2$ catalyst. They have obtained the CO stretching frequencies as a function of temperature. They have observed linear, geminal and bridged CO chemisorbed on surfaces, but a high-frequency component after low-temperature reduction has been observed.

The interaction of carbon monoxide on transition metal clusters has been the subject of several experimental studies [1–6]. The early work by Smalley and co-workers [4] as well as Cox and co-workers [2] were focused on the size dependence of transition metal cluster reactivity with H$_2$ as well as CO. In contrast to H$_2$ reactivity, CO was found to react with most clusters without exhibiting too much size dependence. The Nb metal atom and Nb$_2$ dimer do not exhibit too much reactivity with CO, and this needs explanation. A more recent experimental study by Holmgren et al. [11] employed laser ionization and time-of-flight mass spectrometry (TOF-MS) to detect the reaction products emerging from a beam of Nb clusters passing through a low-pressure reaction cell containing CO. Absolute sticking probabilities of CO as a function of the cluster size were obtained, which revealed that in contrast to earlier work [2,4], the CO reactivity exhibited a strong size dependence, especially for smaller clusters. Similar reactivity studies have been made on Nb clusters with H$_2$ [21]. Recently, organometallic complexes containing niobium and CO ligand have been reported [22,23].

The above survey of experimental studies on the reactivity of CO on transition metal clusters has been the subject of several experimental studies [1–6]. The early work by Smalley and co-workers [4] as well as Cox and co-workers [2] were focused on the size dependence of transition metal cluster reactivity with H$_2$ as well as CO. In contrast to H$_2$ reactivity, CO was found to react with most clusters without exhibiting too much size dependence. The Nb metal atom and Nb$_2$ dimer do not exhibit too much reactivity with CO, and this needs explanation. A more recent experimental study by Holmgren et al. [11] employed laser ionization and time-of-flight mass spectrometry (TOF-MS) to detect the reaction products emerging from a beam of Nb clusters passing through a low-pressure reaction cell containing CO. Absolute sticking probabilities of CO as a function of the cluster size were obtained, which revealed that in contrast to earlier work [2,4], the CO reactivity exhibited a strong size dependence, especially for smaller clusters. Similar reactivity studies have been made on Nb clusters with H$_2$ [21]. Recently, organometallic complexes containing niobium and CO ligand have been reported [22,23].

The above survey of experimental studies on the reactivity of carbon monoxide on transition metal clusters has been the subject of several experimental studies [1–6]. The early work by Smalley and co-workers [4] as well as Cox and co-workers [2] were focused on the size dependence of transition metal cluster reactivity with H$_2$ as well as CO. In contrast to H$_2$ reactivity, CO was found to react with most clusters without exhibiting too much size dependence. The Nb metal atom and Nb$_2$ dimer do not exhibit too much reactivity with CO, and this needs explanation. A more recent experimental study by Holmgren et al. [11] employed laser ionization and time-of-flight mass spectrometry (TOF-MS) to detect the reaction products emerging from a beam of Nb clusters passing through a low-pressure reaction cell containing CO. Absolute sticking probabilities of CO as a function of the cluster size were obtained, which revealed that in contrast to earlier work [2,4], the CO reactivity exhibited a strong size dependence, especially for smaller clusters. Similar reactivity studies have been made on Nb clusters with H$_2$ [21]. Recently, organometallic complexes containing niobium and CO ligand have been reported [22,23].

The above survey of experimental studies on the reactivity of carbon monoxide on transition metal clusters has been the subject of several experimental studies [1–6]. The early work by Smalley and co-workers [4] as well as Cox and co-workers [2] were focused on the size dependence of transition metal cluster reactivity with H$_2$ as well as CO. In contrast to H$_2$ reactivity, CO was found to react with most clusters without exhibiting too much size dependence. The Nb metal atom and Nb$_2$ dimer do not exhibit too much reactivity with CO, and this needs explanation. A more recent experimental study by Holmgren et al. [11] employed laser ionization and time-of-flight mass spectrometry (TOF-MS) to detect the reaction products emerging from a beam of Nb clusters passing through a low-pressure reaction cell containing CO. Absolute sticking probabilities of CO as a function of the cluster size were obtained, which revealed that in contrast to earlier work [2,4], the CO reactivity exhibited a strong size dependence, especially for smaller clusters. Similar reactivity studies have been made on Nb clusters with H$_2$ [21]. Recently, organometallic complexes containing niobium and CO ligand have been reported [22,23].

In the present study, we employ a relativistic complete active space multi-configuration self-consistent field (CASMCSCF) technique to determine the potential surfaces and spectroscopic constants of several electronic states of niobium carbon monoxide. The multi-reference singles + doubles configuration interaction (MRSDCI) computations have been employed to determine the minimum energies, the equilibrium bond lengths as well as other properties of the low-lying states. The CO vibrational frequencies of the NbCO molecule as well as the dissociation energy have been computed. The Mulliken populations were also computed from the wave functions.

2. Method of calculations

Relativistic effective core potentials (RECPs) for the niobium atom that retained the outer 4s$^2$ 4p$^6$ 4d$^4$ 5s$^1$ shells in the valence space together with the optimized (5s5p4d) valence Gaussian basis set for the Nb atom were taken from LaJohn et al. [26]. The carbon and oxygen basis sets and ECPs have been described before elsewhere [17]. In summary, the [4s4p/ 3s3p] valence Gaussian basis sets for C and O were supplemented with one set of 3d functions derived from Dunning and Hay [27], with $\alpha_d = 0.75$ for carbon and $\alpha_d = 0.85$ for oxygen.

The NbCO was computed here in the C$_{2v}$ point group with the z-axis chosen as the C$_2$ axis. We carried out the CASMCSCF calculations for the entire potential energy curves for several electronic states of different spin multiplicities, dissociating into the low-lying spectral terms of the niobium atom [28]. The Nb–CO bond distance was varied
from 1.4 to 8.0 Å for each state, and for each Nb–C distance, the CO distance was optimized. The Nb 4s, 4p, 4d, and 5s orbitals together with the 2s, 2p orbitals of the carbon and oxygen atoms span ten a1, four b1, four b2, and one a2 representations in the C2v group. Among these, the semicore 4s and 4p orbitals of niobium, and the 2s, 2p1, 2p2 orbitals of oxygen were found to be unimportant for the Nb + CO interaction. These orbitals comprise three a1, two b2, two b1, and one a2 representations. Additionally, the highest a1 orbital does not make significant contribution to the low-lying electronic states of NbCO. Consequently, these orbitals were kept inactive, while the remaining orbitals were included in the active space. Suppose that n1 represents the number of inactive orbitals and n2 the number of active orbitals. The CASMCSCF computations included excitations of 9 active electrons in all possible ways among six a1, two b2, two b1, and one a2 orbitals in the active space. The choice of active and inactive spaces which we label n1 = 3, 2, 2, 0 (a1, b2, b1, a2) and n2 = 6, 2, 2, 1, yields the correct Nb + CO dissociation limits and a correct description of the low-lying atomic states of Nb. It is also consistent with the standard description of the valence orbitals for Nb(4d5 5s0), C(2s2 2p2), and O(2s2 2p4).

The MRSDCI calculations, which included single and double excitations from a chosen set of reference configurations, were carried out for the low-lying states. The reference configurations for the MRSDCI computations were chosen from the CASMCSCF calculations with coefficients ≥ 0.05. The CASMCSCF computations included up to 19264 configuration spin functions (CSFs), while the MRSDCI computations included up to 670300 CSFs. All CASSCF/CI calculations were made by using one of the authors’ modified version of ALCHEMY II codes 1 to include RECPs [29].

3. Results and discussion

Table 1 shows a few possible molecular electronic states of Nb–CO that arise from the various low-lying atomic states of the niobium atom and the closed-shell ground state of CO. The energies at the dissociation limits were obtained by setting the distance between niobium atom and CO to 8.00 Å. As can be seen from Table 1, the ground state of Nb is computed as a 5D state arising from the 4d5 5s1 configuration, consistent with the gross atomic Mulliken population of niobium for the sextet states at the dissociation limit, which is 4d5.99 5s1.00. This assignment and the population result are in excellent agreement with the 5D state from the 4d5 5s1 configuration in Moore’s atomic tables [28]. The a1F excited state of Nb arising from the 4d5 5s2 configuration is computed at 417 cm−1 above the ground state at the MRSDCI levels, although at a less accurate zeroth-order CASSCF level, this state is 3402 cm−1 above the ground state. The more accurate MRSDCI result of 417 cm−1 is much closer to the experimental result of 1487 cm−1. The gross atomic Mulliken populations of niobium for the quartet states at the dissociation limit are computed as 4d3 0.02 5s1.89, which are in agreement with the 4d3 5s2 configuration of Nb. The doublet states of NbCO at the dissociation limit are computed to lie 10732 cm−1 above the ground state at the MRSDCI level. Furthermore, a 2 Σ+ state of NbC dissociates into this limit. Thus we attribute this dissociation limit to the 2 G excited state of Nb atom. As seen from Table 1, although the CASSCF method yields excited state energy separations that are too high, the more accurate MRSDCI result (10732 cm−1) is in very good agreement with the experimental result of 8472 cm−1. Our computed Rv and ωv values of the diatomic CO at the dissociation limit obtained from the MRSDCI computations are 1.130 Å and 2133 cm−1, compared to the corresponding experimental values of 1.128 Å and 2170 cm−1, respectively, for the free CO molecule in Ref. [30].

The CASMCSCF potential energy curves for the low-lying electronic states of Nb–CO are presented in Fig. 1. The curves have been generated as a function of the Nb–C separation. It is interesting that the CO equilibrium bond length remains almost unchanged as the bond length of Nb–C varies from 1.3 to 8.00 Å. As seen from Fig. 1 and Table 1, the sextet electronic states dissociate into the Nb(a6D) + CO(3Σ+) dissociation limit, while the quartet and doublet states dissociate into the Nb(a8F) +

1 The major authors of ALCHEMY II are B. Liu, B. Lengsfiled and M. Yoshimine.
Table 1

<table>
<thead>
<tr>
<th>Molecular state</th>
<th>Dissociation limit</th>
<th>CASMCSF (cm⁻¹)</th>
<th>MRSDCI (cm⁻¹)</th>
<th>Expt. (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²Σ⁺, ⁶Π, ⁸Δ</td>
<td>(4d⁴S⁵s)²Σ⁺</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>⁴Φ, ⁴Δ</td>
<td>(4d⁴S⁵s)²Σ⁺</td>
<td>3402</td>
<td>417</td>
<td>1487</td>
</tr>
<tr>
<td>²Σ⁺, ²Π, ²Γ</td>
<td>(4d⁴S⁵s)²Σ⁺</td>
<td>16590</td>
<td>10732</td>
<td>8472</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a The distance between Nb–C is 8.00 Å.
b The experiment data are J-averaged values [28].

CO(²Σ⁺) and Nb(²G) + CO(¹Σ⁺) dissociation limits, respectively.

As evidenced from Fig. 1, the repulsive ⁶Δ and ⁶Π curves cross the bound ⁴Φ and all doublet electronic states of NbCO. This suggests that the bound excited electronic states of NbCO would be predisassociated into the ground state of Nb + CO. A primary mechanism for the pre-dissociation process would be spin–orbit coupling since the spin–orbit contribution to Nb is large enough to assist pre-dissociation of the excited states through this curve crossing.

Table 2 shows the equilibrium geometries (Rₑ), CO vibrational frequencies (ωᵥ), and energy separations (𝑇ₑ) of the bound electronic states of the Nb–CO complex computed at both the CASMCSF and MRSDCI levels. It is evident from our computations that the ground state of NbCO is found to be the ⁶Σ⁺ state at all levels of theory. This differs from TaCO [20], which exhibits two nearly degenerate states (⁶Δ, ⁶Σ⁺) as candidates for the ground state of TaCO. The Rₑ values of the Nb–C and C–O bonds for the ⁶Σ⁺ state are computed as 2.168 and 1.139 Å at the CASMCSF level, respectively, while at the MRSDCI level these bond lengths become 2.124 and 1.146 Å, respectively. The higher-order MRSDCI electron correlation effects shrink the Nb–C bond by 0.044 Å compared to the CASMCSF results. The lowest excited state of NbCO is found to be a ⁴Φ
Table 2
Spectroscopic properties of electronic states of NbCO*

<table>
<thead>
<tr>
<th>State</th>
<th>CASMCSCF</th>
<th>MRSDCI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb–C (Å)</td>
<td>C–O (Å)</td>
</tr>
<tr>
<td>$^6\Sigma^+$</td>
<td>2.168</td>
<td>1.139</td>
</tr>
<tr>
<td>$^4\Phi$</td>
<td>2.035</td>
<td>1.165</td>
</tr>
<tr>
<td>$^4\Delta$</td>
<td>2.139</td>
<td>1.134</td>
</tr>
<tr>
<td>$^2\Pi$</td>
<td>2.023</td>
<td>1.158</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>1.963</td>
<td>1.176</td>
</tr>
</tbody>
</table>

*The $\omega_v$ stands for the vibrational frequencies between C and O atoms. The values in parentheses are the Davidson corrected energies.

state, with the $T_v$ values of 3092 and 2840 cm$^{-1}$ at the MRSDCI and MRSDCI + Q levels, respectively, relative to the $^6\Sigma^+$ ground state. As expected, the $R_e$ value of the C–O bond remains almost the same for different electronic states as well as for the various Nb–C bond lengths, suggesting that the bond strength of CO is not affected too much in the formation of the Nb–CO complex. Our computed CO vibrational frequencies for most of the states are ~2150 cm$^{-1}$. Some other low-lying states are assigned to $^4\Delta$, $^2\Pi$, $^2\Sigma^+$, etc.

The dissociation energies ($D_e$) of the low-lying states with respect to the Nb($^4\text{D}$) + CO($^2\Sigma^+$) dissociation limit are also shown in Table 2. The $D_e$ of the $^6\Sigma^+$ ground state is computed as 0.968 eV at the MRSDCI level, although it considerably lower at the CASSCF level (0.389 eV). This clearly demonstrates the importance of higher-order electron correlation effects for NbCO. The MRSDCI + Q result, which is a full CI estimate reveals that the $D_e$ is 1.11 eV. The fact that the quadruple cluster corrections increase the $D_e$ by only 0.14 eV is quite comforting and seems to indicate that the MRSDCI level is quite converged and accurate. All dissociation energies in Table 2 are given with respect to the Nb ground state since most of the excited states would undergo predissociation, as indicated earlier. With the exception of $^2\Sigma^+$ state, most of the excited electronic states of NbCO are bound relative to Nb($^4\text{D}$) + CO. It is evident from Table 2 that higher-order electron correlation effects have significant effect on the dissociation energies of the excited states. For example, the $D_e$ of the $^2\Phi$ state is computed as -0.059 eV at the CASMCSCF level, but the higher-order MRSDCI lowers the minimum, thus increasing the $D_e$ to 0.585 eV.

Although there are no gas-phase spectroscopic studies on the NbCO molecule, there are a few experimental studies on the reactivity of niobium clusters with CO [2,4,11]. A recent study by Holmgren et al. [11] has revealed that the reactivity of niobium clusters with CO exhibits strong size dependence for smaller clusters. There have been previous studies by Smalley and co-workers [4] as well as Cox et al. [2]. All these studies seem to suggest that clusters containing three or more atoms react readily with CO. Most of such TOF-MS studies do not find that the atom and dimer react with CO. This is surprising for niobium in view of the computed dissociation energy of 1.11 eV, which should be large enough to observe the molecule in the gas phase. However, in the TOF-MS experiments, there are several critical factors for the observation of chemisorbed CO, namely the sticking probability of CO on the cluster and the presence of a thermalising buffer gas. The smaller clusters, especially the dimer and the atom may not be able to accommodate the chemisorption heat and lead to the formation of stable products in the absence of such a thermalising buffer gas, which could stabilize the complex.

Our computed CO stretching frequency could be compared with the atop chemisorbed CO stretching frequencies on surfaces. Beutel et al. [10] have studied the CO hydrogenation on Nb-oxide-promoted Rh/SiO$_2$ catalyst. They found that the stretching frequency for the linear CO ligand to be 2077 cm$^{-1}$ on Nb-promoted Rh/SiO$_2$ catalyst at 573 K followed by reduction at 673 K. Our computed CO
stretching frequency for the NbCO complex is 2135 cm\(^{-1}\), as seen from Table 2 at the MRSDCI level of theory.

Table 3 shows the leading configuration in the MRSDCI wave functions of the low-lying electronic states of Nb±CO, where only the outermost 9 active electrons are shown. As seen from Table 3, with the exception of the \( ^2\Pi \) excited electronic state, most of the electronic states are predominantly represented by a single leading configuration. The \( ^6\Sigma^+ \) ground state is composed of 1\( \sigma^2 \) 2\( \sigma^2 \).3\( \sigma^1 \) 1\( \pi^2 \) 1\( \delta^5 \) with a coefficient of 0.92, while the lowest \( ^4\Phi \) excited state is formed from the \( ^6\Sigma^+ \) ground state by exciting an electron from the 1\( \delta \) orbital to 1\( \pi \) orbital. The \( ^4\Delta \) low-lying state is formed from the \( ^6\Sigma^+ \) ground state by exciting an electron from the 1\( \delta \) orbital to 3\( \sigma \) orbital.

Most interesting information on the nature of bonds in the various electronic states of NbCO is obtained from the Mulliken populations of the low-lying states presented in Table 4. Note that in Table 4, the semi-core 4s\(^2\) 4p\(^6\) shells of Nb are included in the populations. The Mulliken populations on oxygen (6.478–6.547) are almost unchanged for different electronic states. Since the net atomic charge on oxygen is around 0.5e, this is balanced by a corresponding deficiency in the electronic charge density on carbon and niobium. The standard description of bonding of M + CO is one of donation of electronic density from the highest occupied \( \sigma \) orbital of CO to the metal atom, followed by a back donation from the metal atom’s d orbital to the carbonyl \( \pi^* \) antibonding orbital, which has a large carbon component. As seen from Table 4, the \( ^6\Sigma^+ \) ground state of NbCO is composed of O(2s\(^1\).923\(^-\), 2p\(^4\).508\(^+\)), C(2s\(^1\).541 \( ^2\)p\(^2\).230\(^+\)), and Nb(4s\(^2\).802 \( ^2\)p\(^6\).000 \( ^3\)d\(^8\).852\(^+\)). Compared with the gross population of Nb + CO at the dissociation limit, which is O(2s\(^1\).821 \( ^2\)p\(^4\).460\(^+\)), C(2s\(^1\).756 \( ^2\)p\(^1\).830\(^+\)), and Nb(3.001 \( ^2\)p\(^5\).010 \( ^3\)d\(^3\).989\(^+\)), there is a transfer of 0.22e electron from the carbon 2s orbital to the niobium in the formation of Nb–CO bond. Niobium in turn feeds back \( \sim 0.14e \) charge from its d\( \pi^* \) orbital to the p\( \pi^* \) orbital of CO, while the 5s orbital loses 0.2e along the z-axis. The propensity of the niobium atom to donate electrons toward the carbon site determines the strength of the Nb–C bond. Consequently, the net population of niobium has decreased by \( \sim 0.34e \), while the carbon and oxygen populations increase by \( \sim 0.15e \) and \( \sim 0.19e \), respectively. Thus in the case of the \( ^6\Sigma^+ \) ground state, both the \( \sigma \) and p\( \pi^* \)–d\( \pi^* \) bonds play an important role.

It is interesting to note that the Nb population in the ground state of NbCO (Nb: 2.802 \( ^2\)s\(^6\).007 \( ^3\)d\(^1\).852\(^+\)) is close to the Nb atomic electronic configuration of \( ^4\Sigma^+ \) 4s\(^2\) 4p\(^6\) 4d\(^4\) 5s\(^1\) in the \( ^6\)D ground state, but the smaller s and d populations of Nb in NbCO are fully consis-

**Table 3**

<table>
<thead>
<tr>
<th>State</th>
<th>Coefficients (%)</th>
<th>Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^6\Sigma^+ )</td>
<td>92</td>
<td>2 2 1 0 2 2</td>
</tr>
<tr>
<td>( ^4\Phi )</td>
<td>87</td>
<td>2 2 1 0 3 1</td>
</tr>
<tr>
<td>( ^4\Delta )</td>
<td>82</td>
<td>2 2 2 0 2 1</td>
</tr>
<tr>
<td>( ^2\Pi )</td>
<td>62</td>
<td>2 2 2 0 3 0</td>
</tr>
<tr>
<td>( ^2\Sigma^+ )</td>
<td>7</td>
<td>2 2 0 0 3 2</td>
</tr>
<tr>
<td>( ^4\Gamma )</td>
<td>87</td>
<td>2 2 2 0 2 1</td>
</tr>
<tr>
<td>( ^4\Pi )</td>
<td>97</td>
<td>2 2 1 1 1 2</td>
</tr>
<tr>
<td>( ^4\Delta )</td>
<td>97</td>
<td>2 2 1 1 2 1</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>State</th>
<th>Gross atomic population</th>
<th>Gross orbital population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>( ^6\Sigma^+ )</td>
<td>6.478</td>
<td>3.861</td>
</tr>
<tr>
<td>( ^4\Phi )</td>
<td>6.520</td>
<td>3.934</td>
</tr>
<tr>
<td>( ^4\Delta )</td>
<td>6.451</td>
<td>3.790</td>
</tr>
<tr>
<td>( ^2\Pi )</td>
<td>6.499</td>
<td>3.857</td>
</tr>
<tr>
<td>( ^2\Sigma^+ )</td>
<td>6.547</td>
<td>3.884</td>
</tr>
</tbody>
</table>

\(^4\)s\(^2\) 4p\(^6\) shells of Nb atom are included in the Mulliken populations.
tent with the charge transfer from Nb to CO. On the other hand, the excited electronic states such as $^4\Phi$ deviate considerably from the corresponding Nb atomic populations. For example, the $^4\Phi$ state has a Nb population of $s^2 4p^6 4d^3 5s^2$, which differs from the corresponding atomic Nb electronic configuration of $4s^2 4p^6 4d^3 5s^2$ of the $^4\Phi$ state of Nb. This explains the reason for larger differences in the computed properties at a lower level of theory (CAS-SCF) compared to a higher level (MRSDCI), since the lower level does not provide adequate rearrangement of electron density due to the limited inclusion of electron correlation effects. Furthermore, the $D(4d^4 5s^1)$ electronic configuration of Nb cannot form appreciable bonding with CO due to the closed shell of the $5s$ orbital. The promotion of an electron from $5s$ to $4d$ would be necessary for the formation of the Nb–CO bond, and this is reflected in the Mulliken populations. On the other hand, the $^4\Phi$ excited state exhibits a lower Nb(4d) population of 3.201 and an increased Nb(5s) population of 1.492, suggesting mixed Nb(4s$^2 4p^6 4d^3 5s^2$) and Nb(4s$^2 4p^6 4d^4 5s^1$) character in this state. The electronic charge transfer from Nb to CO is larger in the case of $^4\Phi$ compared to the $^6\Sigma^+$ ground state.

It is interesting to compare the computed properties and the nature of bonding of NbCO with other transition metal–Co complexes. Majumdar and Balasubramanian [20] have studied the electronic states of TaCO, and since Ta and Nb are in the same column of the periodic table it will be worthwhile to compare the two species. For TaCO the previous study finds a $^4\Delta$ state as the ground state but a $^6\Sigma^+$ state is only 691 cm$^{-1}$ above the $^4\Delta$ state. The next low-lying excited state is a $^2\Pi$ state at 2709 cm$^{-1}$. The Ta–C bond distances in the $^6\Sigma^+$, $^4\Delta$, and $^2\Pi$ states are 2.079, 2.063, and 1.992 Å, respectively. The CO vibrational stretching frequencies are 2239(MP2) and 1947(MP2) (MRSDCI: 2151 cm$^{-1}$) for the $^4\Delta$ and $^6\Sigma^+$, respectively. These properties can be compared with the values in Table 2 for NbCO. The Nb–C distances are uniformly longer than the Ta–C distances of the corresponding electronic states. The CO stretching frequencies are not too different for NbCO and TaCO at the same level of theory. Thus the major differences are in the relative ordering of electronic states and the Ta–C and Nb–C distances. The shorter Ta–C distances, in contrast to our expected trend as one goes down the column of the periodic table, can be explained on the basis of relativistic effects. The relativistic mass-velocity contraction of the $6s$ orbital of Ta contracts the Ta–C bond compared to Nb–C bond. As a consequence of the $6s$ orbital stabilization for Ta, the ground state of Ta is $^4\Pi(5d^3 6s^2)$, in contrast to the $^6\Delta(4d^4 5s^1)$ ground state of Nb. The $^6\Delta$ state is almost an eV higher for Ta. Thus the quartet electronic states are more stabilized for NbCO compared to TaCO. For example, the $^4\Delta$ state of TaCO is bound by an eV, while the corresponding state of NbCO is bound by only 0.39 eV.

The third-row transition metal atoms form stronger bonds with CO compared to the second-row transition metal atoms. This has been already discussed for NbCO and TaCO. Likewise, the Ir–C distance in Ir–CO is 1.772 Å, while the Rh–C distance is 1.839 Å in RhCO [19]. The binding energies of CO on Ir and Rh are 2.13 and 0.87 eV, respectively. The CO stretching frequencies are lower for the third row due to the stronger metal–C bonds formed by the third-row transition metal atoms.

4. Conclusions

We obtained the potential energy surfaces and spectroscopic properties of the low-lying electronic states for NbCO arising from three dissociation limits, namely, Nb(a$^6\Delta$) + CO($^1\Sigma^+$), Nb(a$^4\Phi$) + CO($^1\Sigma^+$), and Nb(a$^2\Sigma$) + CO($^1\Sigma^+$), respectively. The ground state of NbCO was found to be the $^6\Sigma^+$ state, with a very low-lying $^4\Phi$ excited state. The equilibrium bond lengths for the $^6\Sigma^+$ ground state are Nb–C = 2.124 and C–O = 1.146 Å at the MRSDCI level. The dissociation energy values for all the low-lying states have been calculated. The nature of the low-lying electronic states is discussed through the CI coefficients and the Mulliken populations.

Acknowledgements

This research was supported by the US Department of Energy under Grant No. DEFG02-86ER13558.
References