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Theoretical Study of Ar−CoCO

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It is shown that Ar combines with CoCO (X $^2\Delta$) with the binding energy of 7.18 kcal/mol (CASPT2), 6.25 kcal/mol (RCCSD(T)), and 5.05 kcal/mol (UMPWPW91) in which a counterpoise correction and zero-point vibrational energy correction have been included. The Co−C−O bending frequency has been calculated, by the UMPWPW91 method, as 373.0 and 422.9 cm^{-1} for CoCO and Ar−CoCO, respectively, the latter of which is in good agreement with the corresponding experimental frequency, 424.9 cm^{-1}, determined for CoCO isolated in solid argon.

Introduction

Recently, the first covalent argon compound, HArF, was discovered,[1] which has brought an impact on the noble gas (Ng) chemistry. Evans, Gerry, and co-workers have found that an argon atom makes a stable compound with a coinage metal monohalide, Ar−MX (M = Cu, Ag, Au; X = F, Cl, Br), and determined their geometrical structures by the microwave spectra.[2−5] An ab initio study on these compounds was reported very recently,[6] which shows a qualitative agreement in bond lengths between theory and experiment. Since the lighter noble gases, helium, neon, and argon, are relatively more inactive than the heavier noble gases, it is more difficult to synthesize a stable compound containing the lighter ones in the experiments. There have been several theoretical studies on the possible noble gas compounds of RNBe−Ng[7] (Ng = He, Ne, Ar; R = H, CH_3, OH, F, CH_2OH, CH_2F, COH, COOH, COF, C_6H_5, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3) and SBeNg[8] (Ng = He, Ne, Ar).

Very recently, we have found that an argon atom can combine with NiCO and NiN_2, respectively, with a larger binding energy than expected (7−9 kcal/mol), by applying ab initio multireference theory and density functional theory (DFT) calculations.[9,10] Interestingly, Ni−C−O and Ni−N−N bending frequencies, respectively, increase by 40−50 cm^{-1} (∼10%) due to binding with Ar, resulting in quite good agreement with the corresponding experimental frequencies determined for each compound in solid argon.[11,12] In the matrix isolation infrared spectroscopy, the frequency shifts from the gas phase are considered to be relatively small, typically less than 0.5%.[13] Our results indicate that this assumption breaks down for transition metal compounds isolated in argon matrix in some cases.

According to the recent review on vibrational frequencies in binary unsaturated transition metal carbonyl compounds,[14] most spectroscopic data on the transition metal species have been determined using the matrix-isolation technique. Gutsev et al.[15] carried out DFT calculations for a series of M−CO (M = Sc to Cu), and have described that theoretical M−CO bending frequencies are appreciably lower than the experimental ones. Taking into account our previous studies on Ar−NiCO,[9] the discrepancy in bending frequency between theory and experiment may be attributed to the neglect of effects of Ar in theoretical calculations. Following Ar−NiCO, we have decided to investigate the binding of Ar and CoCO (X $^2\Delta$) in the present study.

The vibrational frequencies of the CoCO molecule have been reported by Zhou and Andrews,[16,17] and by Tremblay et al.,[18] both of which have been determined by noble gas matrix isolation technique. Tremblay et al.[18] reported all the fundamental frequencies of CoCO and several isotopomers determined in solid argon. Theoretically all previous calculations on CoCO were carried out by several DFT methods.[15−21] We apply ab initio highly correlated methods, as well as a DFT method, to determine geometries and frequencies of CoCO and Ar−CoCO, and compare the results with the experimental frequencies determined in solid argon.

Computational Details

Geometry optimizations were carried out for the X $^2\Delta$ state of CoCO by the second-order multireference perturbation theory (CASPT2)[22] and the restricted open-shell coupled-cluster singles and doubles including a perturbational estimate of triple excitations (RCCSD(T))[23] methods. As the CASPT2 method, we have used a modified version developed by Celani and Werner,[22] which is referred to as “RS2C” in the Molpro program.[24] In CASPT2 calculations, the state-averaged complete active space self-consistent field (SA-CASSCF) wave function was determined initially as the reference wave function, with the active space of 3d and 4s of Co and 5σ, 6σ, 1π, and 2π of CO (15 electrons in 12 orbitals). In SA-CASSCF calculations two degenerate states of Δ (A_1 and A_2 in the C_{2v} point group) were averaged with equal weights, while RCCSD(T) calculations were carried out for the A_2 state in C_{2v}. Geometry optimizations were also performed for Ar−CoCO at the

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TABLE 1: Calculated Equilibrium Bond Lengths (in Å) for CoCO and Ar−CoCO and the Binding Energy (BE in kcal/mol) between Ar and CoCO

	CoCO		Ar−CoCO			
	r(CoC)	*r*(CO)	*r*(ArCo)	*r*(CoO)	*r*(CO)	BE
CASPT2	1.668	1.171	2.340	1.677	1.172	8.14
RCCSD(T)	1.684	1.162	2.351	1.670	1.166	7.21
UMPWPW91	1.666	1.167	2.354	1.679	1.167	6.01

CASPT2 and RCCSD(T) levels. All the CASPT2 and RCCSD(T) calculations were carried out by the Molpro program.[24]

We also performed DFT calculations with the modified Perdew-Wang 1991 exchange by Adamo and Barone[25] plus Perdew-Wang 1991 correlation based on spin-unrestricted orbitals (UMPWPW91)[26] for CoCO and Ar−CoCO, using the Gaussian 98 program.[27] The MPWPW91 functionals were shown to give very good results for Ng−NiCO[9] and Ng−NiN$_2$,[10] compared to other functionals, so we employed these functionals in the present study. The options, "scf = tight", "grid = ultrafine", and "opt = tight", were employed throughout. Harmonic frequencies were calculated analytically by the UMPWPW91 method where the atomic masses were set to those of the most probable species (^{59}Co, ^{12}C, ^{16}O,^{40}Ar). The isotopic shifts were also investigated.

As to basis sets, aug-cc-pVTZ[28,29] was employed for C, O, and Ar, while the relativistic pseudopotentials of the Stuttgart/Cologne group (for Ne-core) and related basis functions of (8s7p6d1f)/[6s5p3d1f] for 3s, 3p, 3d, 4s valence electrons (referred to as ECP10MDF)[30] were employed for Co.

Results and Discussion

In 3d-metal monocarbonyls, the electronic ground state has a multiconfigurational character because of the incomplete occupation in d orbitals. The electronic ground state of CoCO is $^2\Delta$, which originates from the excited state of Co, ^{2}F with 3d^{8}4s^1. In SA-CASSCF calculations for the X $^2\Delta$ state of CoCO, the energies for A_1 and A_2 states were calculated as the same value, and the weights of the dominant electronic configuration were calculated, respectively, as 80%. The corresponding weight for X $^2\Delta$ state of Ar−CoCO was evaluated as a slightly larger value, 81%. The norm for the RCCSD wave function for X $^2\Delta$ state of CoCO gets a large value of 1.7 at the optimized structure, where the norm corresponds to the relative rate of the RCCSD wave function to the reference Hartree−Fock wave function. Such a large norm indicates that RCCSD(T) gives not so good descriptions for the electronic structure of CoCO. On the other hand, the norm for the RCCSD wave function for Ar−CoCO has been reduced to 1.4, indicating the reduction of multiconfigurational character in Ar−CoCO.

Geometrical parameters of the equilibrium geometry of CoCO and Ar−CoCO and the binding energy (BE) for Ar and CoCO determined by CASPT2, RCCSD(T), and UMPWPW91 methods are given in Table 1. The equilibrium Co−C bond length for CoCO (X $^2\Delta$) determined by the CASPT2, RCCSD(T), and UMPWPW91 methods are 1.668, 1.684, and 1.666 Å, respectively, and thus, RCCSD(T) predicts a longer bond length than other methods. Present calculations verified that Ar−CoCO takes a linear equilibrium structure. The Ar−Co bond distance is evaluated as 2.340, 2.351, and 2.354 Å at the CASPT2, RCCSD(T), and UMPWPW91 levels, respectively. Due to the bonding of Ar and CoCO, the CoC bond length becomes longer by ca. 0.01 Å while the CO bond length is almost unchanged, indicating that the Co−C bond becomes slightly weakened in Ar−CoCO at the CASPT2 level. The UMPWPW91 values are in good agreement with the corresponding CASPT2 values despite multi-configurational character in the electronic structure. This tendency is also seen in the previous study on Ar−NiCO[9] and Ar−NiN$_2$.[10]

TABLE 2: Natural Atomic Orbital Populations in Valence Orbitals, Net Charges (*Q*), and Dipole Moments *μ* (in Debye) for Co−C−O and Ar−Co−C−O Derived from Natural Population Analyses for UMPWPW91 Results

	Co					C					O					Ar				
	4s	3d	5s	4d	Q	2s	2p	3s	3p	Q	2s	2p	3s	3p	Q	3s	3p	3d	Q	*μ*
CoCO	0.83	8.07	0.01	–	+0.10	1.27	2.32	0.02	0.02	+0.36	1.71	4.71	0.01	0.03	−0.47					3.27
Ar−CoCO	0.82	8.15	0.01	0.01	−0.01	1.29	2.30	0.02	0.02	+0.36	1.71	4.72	0.01	0.03	−0.44	1.97	5.92	0.01	+0.09	4.60

The binding energy for Ar−CoCO was evaluated as a difference between the energy of Ar−CoCO and a sum of energies of Ar and CoCO by RCCSD(T) and UMPWPW91 methods, while it was evaluated as the energy difference between Ar−CoCO and Ar···CoCO with the Ar−Co distance of 50 Å by the CASPT2 method: BE(CASPT2) = 8.14 kcal/mol; BE(RCCSD(T)) = 7.21 kcal/mol; BE(UMPWPW91) = 6.01 kcal/mol. These binding energies indicate that Ar−CoCO is more strongly bound than typical van der Waals complexes. A similar binding energy was evaluated for Ar−NiCO and Ar−NiN$_2$ in our previous study,[9,10] and for Ar−FeCO by Zhou and Andrews.[31]

In the estimation of the binding energy, it is important to take into account corrections for the zero-point vibrational energy (ZPE) and the basis set superposition error (BSSE), the latter of which is caused by the unbalance in numbers of basis functions in electronic structure calculations. The ZPE corrections can be included by subtracting the difference of ZPE's for Ar−CoCO and CoCO from the binding energy, while the BSSE can be corrected by the counterpoise correction (CP) method.[32] Taking into account change of CoCO geometry in CoCO and Ar−CoCO, the BSSE-corrected binding energy was evaluated by the UMPWPW91 method as

$$\mathrm{BE}_{\mathrm{CP}} = E(\mathrm{Ar})^* + E(\mathrm{CoCO})^{\#,*} - E(\mathrm{Ar{-}CoCO}) + E(\mathrm{CoCO}) - E(\mathrm{CoCO})^{\#} \quad (1)$$

where E(A)* denotes the energy for fragment A determined with all the basis functions for Ar−CoCO, and E(CoCO)$^{\#}$ denotes the energy for CoCO of which geometry is fixed to those in Ar−CoCO. The BSSE-corrected binding energy was evaluated as 5.64 kcal/mol. By including ZPE corrections, this value has been further reduced to 5.05 kcal/mol (UMPWPW91) where ZPE was estimated from harmonic frequencies. By applying the ZPE and counterpoise corrections from the UMPWPW91 calculations to the CASPT2 and RCCSD(T) results, the corresponding binding energies are estimated as 7.18 kcal/mol (CASPT2) and 6.25 kcal/mol (RCCSD(T)). Therefore, these corrections do not change the result that Ar and CoCO combine with a larger binding energy than expected.

Table 2 shows natural atomic orbital populations and net charges for Co−C−O and Ar−Co−C−O derived from natural population analyses[33] for UMPWPW91 results. In CoCO, part of the electrons (∼0.10) in Co (3d^{8}4s^1) are transferred to the CO part where net charges of C and O are evaluated as +0.36 and −0.47, respectively. Due to the binding of Ar and CoCO, part of the electrons (∼0.09) of Ar are transferred to 3d orbitals

TABLE 3: Calculated Harmonic Frequencies (in cm^{-1}) and Absolute IR Intensities (in km/mol) in Parentheses for CoCO and Ar−CoCO at the UMPWPW91 Level

	ν(CO)	ν(CoC)	ν(CoCO)	ν(ArCo)	ν(Ar−CoCO)
CoCO	1979.1(775)	599.2(11)	373.0(16)		
Ar−CoCO	1983.3(737)	594.2(5)	422.9(6)	167.6(0.0)	72.5(0.5)
exp[a]	1957.5(860)	579.2(2)	424.9(8)		

[a] Experimental fundamental frequencies for CoCO isolated in solid argon.[18]

TABLE 4: Reduced Masses (in amu) and Force Constants (in mdyne/Å) of the Respective Normal Modes of CoCO and Ar−CoCO, Calculated at the UMPWPW91 Level

CoCO	ν(CoC)	ν(CO)	ν(CoCO)
reduced mass	18.941	13.242	12.922
force constant	4.007	30.559	1.059

Ar−CoCO	ν(CoC)	ν(CO)	ν(CoCO)	ν(ArCo)	ν(Ar−CoCO)
reduced mass	18.917	13.233	13.099	35.856	29.948
force constant	3.936	30.669	1.380	0.593	0.093

of Co. Such an electron transfer can be invoked by the low-lying 3d orbitals of Co. Atomic orbital populations for the CO part in Ar−CoCO are less affected. The dipole moment in Ar−CoCO changes largely from that of CoCO, which is also caused by the electron transfer from Ar to Co.

Table 3 shows harmonic frequencies and the absolute IR intensity (in parentheses) for CoCO and Ar−CoCO calculated by the UMPWPW91 method, with the experimental fundamental frequencies and intensities of CoCO isolated in argon matrix.[18] The frequencies, ν(CO), ν(CoC), and ν(ArCo), correspond to C−O, Co−C, and Ar−Co stretching modes, respectively, while ν(CoCO) and ν(Ar−CoCO) correspond to Co−C−O and Ar−CoCO bending modes, respectively. The Co−C−O bending mode consists of bending motion of Co−C−O fragment, while the Ar−CoCO bending mode consists of rotational motion of CoCO relative to Ar. The comparison of the frequencies of Ar−CoCO with those of CoCO shows that the Co−C−O bending frequency is largely shifted (increase of ca. 50 cm^{-1} (13%) in Ar−CoCO), while changes in the frequencies of Co−C and C−O stretching modes are relatively small. The experimentally estimated harmonic frequency of ν(CO) is 1957.5 cm^{-1},[18] which is close to corresponding frequencies of 1979.1 cm^{-1} (CoCO) and 1983.3 cm^{-1} (Ar−CoCO) at the UMPWPW91 level. Table 4 shows reduced masses and force constants of the respective normal modes of CoCO and Ar−CoCO calculated by the UMPWPW91 method. The reduced masses in Ar−CoCO are almost unchanged in comparison with those in CoCO, while the force constant for ν(CoCO) increases largely from 1.059 (in CoCO) to 1.380 (in Ar−CoCO) mdyne/Å, which work to increase the frequency. This change of force constant can be related to the movement of each atom in the ν(CoCO) mode where an Ar−Co bond distance increases. According to changes in force constants, the CoC bond becomes slightly weakened while the CO bond becomes slightly strengthened in Ar−CoCO. This tendency coincides with the cases of NiCO and Ar−NiCO.[9]

TABLE 5: Isotopic Shifts (in cm^{-1}) of UMPWPW91 Harmonic Frequencies for the Various Isotopomers of CoCO and Ar−CoCO

CoCO	ν(CO)	ν(CoC)	ν(CoCO)	ν(ArCo)	ν(Ar−CoCO)
^{59}Co^{12}C^{18}O					
CoCO	−41.0	−15.8	−4.2		
Ar−CoCO	−40.9	−15.7	−3.6	−0.6	−1.3
exp[a]	−40.1	−15.0	−3.7		
^{59}Co^{13}C^{16}O					
CoCO	−48.4	−5.7	−11.3		
Ar−CoCO	−48.7	−5.7	−13.1	−0.3	0.0
exp[a]	−47.2	−5.3	−13.2		
^{59}Co^{13}C^{18}O					
CoCO	−90.8	−20.7	−15.6		
Ar−CoCO	−90.9	−20.6	−16.8	−0.9	−1.3
exp[a]	−88.5	−19.5	−17.0		

[a] Experimental isotopic shifts determined in solid argon.[18]

The experimental frequencies were those determined for CoCO isolated in solid argon.[18] Since Ar−CoCO has a considerable binding energy as discussed above, there is a possibility that these experimental frequencies are attributed not to CoCO but to Ar−CoCO. The most distinguished change between CoCO and ArCoCO appears in the Co−C−O bending frequency. As shown in Table 3, the experimental frequency for ν(CoCO) is 424.9 cm^{-1}, which is almost the same as the corresponding UMPWPW91 frequency, 422.9 cm^{-1}, for Ar−CoCO; the corresponding UMPWPW91 frequency for CoCO is 373.0 cm^{-1}. This result supports the attribution of the experimental spectrum to Ar−CoCO. Of course, the experimental frequency corresponds to the fundamental affected by the anharmonicity, while the calculated one corresponds to the harmonic frequency. In the review on transition metal carbonyl complexes, however, it is written that "DFT yields a good description of the bonding in these systems and, more specifically, gives harmonic frequencies that are in good agreement with the experimental fundamentals".[14] In Ar−CoCO, there are additional vibrational modes of ν(ArCo) (~167.6 cm^{-1}) and ν(Ar−CoCO) (~72.5 cm^{-1}), but their intensity may be too small to be observed in the experimental spectrum.

Table 5 shows isotopic shifts of vibrational frequencies for CoCO (^{59}Co^{12}C^{16}O, ^{59}Co^{13}C^{16}O, ^{59}Co^{12}C^{18}O, ^{59}Co^{13}C^{18}O) and Ar−CoCO (^{40}Ar^{59}Co^{12}C^{16}O, ^{40}Ar^{59}Co^{13}C^{16}O, ^{40}Ar^{59}Co^{12}C^{18}O, ^{40}Ar^{59}Co^{13}C^{18}O) by the UMPWPW91 method with the corresponding experimental values.[18] As is clearly shown, isotopic shifts in Ar−CoCO are in better agreement with the corresponding experimental values, respectively, than those in CoCO. These results also support the attribution of experimental frequencies in ref 18 to Ar−CoCO.

Conclusions

We have recently shown that an Ar atom can combine with NiCO and NiN$_2$, respectively, with a larger binding energy than the typical van der Waals interactions.[9,10] The bending frequencies in Ar−NiCO and Ar−NiN$_2$ increase by ca. 10% from those in NiCO and NiN$_2$, and the calculated frequencies are in good agreement with the corresponding fundamental frequencies determined for NiCO and NiN$_2$, respectively, in solid argon. In the present paper, we have investigated the binding of Ar and CoCO by the same approaches, and verified that Ar−CoCO can also have a sufficient binding energy of 5−7 kcal/mol which was estimated by including both counterpoise and ZPE corrections. The binding between Ar and CoCO was explained by the electron transfer from an Ar atom to low-lying 3d vacant orbitals of Co atom. Due to the bonding with an Ar atom, the Co−C−O bending frequency increases by ca. 50 cm^{-1}, and the experimental frequency (424.9 cm^{-1}) is much closer to the calculated frequency for Ar−CoCO (422.9 cm^{-1}) than that for CoCO (373.0 cm^{-1}). The isotopic shifts for several isotopomers also show that the experimental values are closer to those calculated for Ar−CoCO than for those of CoCO.

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