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Theoretical Study of Chemical Binding of Noble Gas Atom and Transition Metal Complexes: *Ng*–NiCO, *Ng*–NiN$_2$, *Ng*–CoCO (*Ng* = He–Xe)

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Summary. *Ab initio* multireference and coupled cluster methods (MR-SDCI(+Q), CASPT2, CCSD(T)) and density functional theory methods (*B*3*LYP*, M*PWPW*91) have been applied to examine geometrical structures and vibrational frequencies of noble gas (*Ng*) – transition metal compounds, *Ng*–NiCO, *Ng*–NiN$_2$, and *Ng*–CoCO (*Ng* = He, Ne, Ar, Kr, Xe). It is shown that the respective compounds can have a larger binding energy than a typical *van der Waals* interaction energy. The binding mechanism is explained by a partial electron transfer from a noble gas atom to the low-lying 4s and 3d vacant orbitals of the transition metal atom. Theoretical calculations show that the binding of noble gas atom results in a large shift of the bending frequency: 361.1 cm^{-1} (NiCO) to 403.5 cm^{-1} (Ar–NiCO); 308.5 cm^{-1} (NiN$_2$) to 354.8 cm^{-1} (Ar–NiN$_2$); 373.0 cm^{-1} (CoCO) to 422.6 cm^{-1} (Ar–CoCO). The corresponding experimental frequencies determined in solid argon are 409.1 cm^{-1} (NiCO), 357.0 cm^{-1} (NiN$_2$), and 424.9 cm^{-1} (CoCO), which are much closer to the corresponding frequency of Ar–NiCO, Ar–NiN$_2$, and Ar–CoCO, respectively.

Keywords. Noble gas compound; Frequency shift.

Introduction

Noble gas (*Ng*) atoms are inactive because of the complete closed-shell electronic structure. Although several compounds containing a heavier noble-gas, radon, xenon, or krypton, have been synthesized [1], the synthesis of compounds containing the lighter noble gas, argon, neon, or helium, has been considered to be impossible. Therefore, discovery of the first covalent argon compound, HArF, has

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brought an impact on the noble gas chemistry [2]. *Evans*, *Gerry*, and coworkers 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 [3–6]. An *ab initio* study on these compounds was reported recently [7], which shows a qualitative agreement in bond lengths between theory and experiment. There have been several theoretical studies on the possible noble gas compounds of RNBe-Ng ($Ng =$ 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) [8] and SBeNg ($Ng =$ He, Ne, Ar) [9].

In a series of recent papers, we have reported that an argon atom can combine with NiCO [10], NiN_2 [11], and CoCO [12], respectively, with a relatively larger binding energy than a typical *van der Waals* binding energy, by applying *ab initio* multireference theory and density functional theory (DFT) calculations. Interestingly, the bending frequency of these compounds increases by 40–50 cm^{-1} ($\sim$10%) due to binding with Ar, resulting in quite good agreements with the corresponding experimental frequencies determined for each compound in solid argon by *Manceron* and coworkers [13–15]. In the matrix isolation infrared spectroscopy, the frequency shifts from the gas phase are considered to be relatively small, typically less than 0.5% [16]. Our results indicate that this assumption breaks down for some transition metal compounds.

The matrix isolation infrared spectroscopy has been a powerful tool to obtain rovibrational spectra of transient molecules. The transient molecules isolated in noble-gas matrices can be produced and accumulated over a long period of time, so detection sensitivity can be enhanced and a broad spectral range can be easily explored in a short time. Also, the absorptions of matrix-isolated species are sharp with many structure-specific features. This methodology is based on the non-reactivity of the noble gases, and the experimental fundamentals determined in the noble gas matrices have been treated as those of the target molecules. According to the recent review on vibrational frequencies in binary unsaturated transition metal carbonyl compounds [17], most spectroscopic data on the transition metal species have been determined using the matrix-isolation technique. *Gutsev et al.* [18] 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.

The electronic structure of a small compound including the first-row transition metal as Ni and Co has a multi-configurational character due to the incomplete occupation of 3d atomic orbitals. For such compounds a multi-configurational method should be applied for qualitative descriptions of electronic states, and also a multireference method should be applied for quantitative discussions of the energetics in *ab initio* theory. On the other hand, the DFT methods have been applied to such multiconfigurational system successfully. In the present paper, we provide all the data related to *ab initio* multireference and DFT calculations on NiCO, NiN_2, CoCO, and their complexes with noble gas atoms, He, Ne, Ar, Kr, Xe. Based on these results, we propose that spectroscopic data of transition metal compounds determined with the matrix isolation technique should be reinvestigated more carefully, taking into account the possibility that the target molecule makes a compound with noble gas atoms.

Computational Details

The target molecules of transition metal compounds have a multi-configurational character in electronic structure. Thus, we applied both *ab initio* multireference methods and DFT methods to examine the applicability of DFT methods. Two *ab initio* multireference methods, the multireference singles and doubles configuration interaction plus *Davidson*'s correction (MR-SDCI(+Q)) [19, 20] and the second-order multireference perturbation theory (CASPT2) [21], the coupled-cluster singles and doubles including a perturbational estimate of triple excitations (CCSD(T)) [22] method, and DFT methods using the hybrid density functional consisting of *Becke*'s three parameter nonlocal hybrid exchange potential with the nonlocal correlation functional of *Lee*, *Yang*, and *Parr* (*B*3*LYP*) [23], and the modified *Perdew-Wang* 1991 exchange by *Adamo* and *Barone* [24] plus *Perdew-Wang* 1991 correlation (M*PWPW*91) [25], have been applied to the determination of equilibrium geometries and vibrational frequencies for NiCO (X $^1\Sigma^+$), NiN_2 (X $^1\Sigma^+$), CoCO (X $^2\Delta$), *Ng*–NiCO (X $^1\Sigma^+$), *Ng*–NiN_2 (X $^1\Sigma^+$), and *Ng*–CoCO (X $^2\Delta$) ($Ng =$ He, Ne, Ar, Kr, Xe). As the CASPT2 method, we have used a modified version implemented in the Molpro program in which subspaces of the singly external and internal configuration spaces are internally contracted (referred to as RS2C in Molpro) [21]. Since the ground state of CoCO and *Ng*–CoCO is doubly degenerate, $^2\Delta$ (corresponding to A_1 and A_2 in the C_{2v} point group), we applied a two-state averaged multiconfigurational SCF (MCSCF) wavefunction as the reference wavefunction for MR-SDCI and CASPT2 calculations, and applied the spin-restricted open-shell CCSD(T) (RCCSD(T)) [26] method and the spin-unrestricted M*PWPW*91 (UM*PWPW*91) method to the one of degenerate state (A_2 in C_{2v}). As to basis sets, aug-cc-pVTZ [27, 28] was employed for C, O, N, He, Ne, Ar, and Kr, while the relativistic pseudopotentials of the Stuttgart/Köln group and related basis functions were employed for Ni and Co (referred to as ECP10MDF) [29] and for Xe (referred to as aug-cc-pVTZ-PP) [30]. All the MR-SDCI(+Q), CASPT2, and CCSD(T) calculations were carried out by the Molpro program [31], while DFT calculations were carried out by using the Gaussian03 program [32].

In the MR-SDCI and CASPT2 calculations, the complete active space self-consistent field (CASSCF) wavefunction was determined initially as the reference wavefunction. As the active space for the CASSCF wavefunction, 3d and 4s of Ni and 4σ, 5σ, 6σ, and 1π of CO have been included (16 electrons in 11 orbitals) for NiCO, 3d and 4s of Ni and $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, and $1\pi_u$ of N_2 (16 electrons in 11 orbitals) for NiN_2, and 3d and 4s of Co and 5σ, 6σ, 1π, and 2π of CO (15 electrons in 12 orbitals) for CoCO.

In DFT calculations the options, "scf = tight" and "opt = tight," were employed throughout, which tighten the criterion of convergence in SCF calculations and geometry optimizations, respectively. Harmonic frequencies were calculated analytically by the M*PWPW*91 method where the atomic masses were set to those of the most probable species. The isotopic shifts were also investigated. To get insight into the bonding mechanism between *Ng* and transition metal compounds, we also investigated natural atomic orbital populations and net charges for the respective compounds derived from natural population analyses [33] for M*PWPW*91 results.

The binding energy for *Ng* and a transition metal compound was evaluated as a difference between the energy of *Ng*-complex and a sum of energies of *Ng* and the transition metal compound by the CCSD(T) and DFT methods, while it was evaluated as the energy difference between *Ng*-complex and the corresponding supermolecule with the $Ng \cdots M$ distance of 50 Å by the CASPT2 method. 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 BSSE can be corrected by the counterpoise correction (CP) method [34]. For example, the BSSE-corrected binding energy for *Ng*–NiCO was evaluated as shown in Eq. (1) where $E(\mathrm{A})^*$ denotes the energy for fragment A determined with all the basis functions for *Ng*–NiCO, and $E(\mathrm{NiCO})^{\#}$ denotes the energy for NiCO of which geometry is fixed to that in *Ng*–NiCO.

$$\mathrm{BE}^{\mathrm{CP}} = E(Ng)^* + E(\mathrm{NiCO})^{\#,*} - E(Ng\mathrm{NiCO}) + E(\mathrm{NiCO}) - E(\mathrm{NiCO})^{\#} \quad (1)$$

In DFT calculations we determined the equilibrium geometry and vibrational frequency based on the CP corrected binding energy using a new option [35] implemented in Gaussian03 [32].

Results and Discussion

Ng–NiCO

The nickel atom has an electronic configuration of $3\mathrm{d}^8 4\mathrm{s}^2$ in both the ground $^3\mathrm{F}$ state and the first excited $^1\mathrm{D}$ state. In NiCO, the degeneracy for the respective triplet and singlet states in nickel are partially broken due to the symmetry-reduction, resulting in the near degenerate manifold of electronic states of triplet, $^3\Phi$, $^3\Delta$, $^3\Pi$, $^3\Sigma^-$, and of singlet, $^1\Delta$, $^1\Pi$, and $^1\Sigma^+$. The term of the ground state of NiCO is $^1\Sigma^+$ with no degeneracy, which originates from the excited state of Ni, $^1\mathrm{D}$ with $3\mathrm{d}^9 4\mathrm{s}^1$. The electronic structure of NiCO ($X\ ^1\Sigma^+$) was analyzed in detail previously [36]. In NiCO a hybridization takes place in the σ symmetry between $3\mathrm{d}_\sigma$ and 4s orbitals, and then a $3\mathrm{d}^9 4\mathrm{s}^1$ occupation on nickel can very well be described by one closed shell configuration. We have verified that the dominant electronic configuration in $X\ ^1\Sigma^+$ of NiCO is a closed-shell configuration, and that the weight of this dominant configuration was 84 and 78% in the CASSCF and MR-SDCI calculations, respectively. Thus, the multi-configurational character is relatively strong in the ground state of NiCO.

Geometrical parameters of the equilibrium geometry of NiCO determined by CASSCF, MR-SDCI(+Q), and CCSD(T) methods are given in Table 1. The dynamical correlation effects work to make the Ni–C bond length shorter (~0.02 Å), and the CO bond length longer (~0.02 Å). The CCSD(T) values are in good agreement with the MR-SDCI(+Q). Table 1 also shows geometrical parameters and binding energies (BE) for *Ng*–NiCO (Ng = He, Ne, Ar) determined by the CCSD(T) method. The normal mode analyses verify that *Ng*–NiCO takes a linear structure as a minimum. As shown in Table 1, these *Ng*–NiCO complexes are more strongly bound than typical *van der Waals* complexes. Especially, Ar and NiCO

Table 1. Equilibrium bond lengths (in Å) for NiCO and *Ng*–NiCO (*Ng* = He, Ne, Ar) determined by CASSCF, MR-SDCI(+Q), and CCSD(T) methods; the binding energies (BE_e in kJ/mol) between *Ng* and NiCO are also given where BE_e and BE_0 denote the binding energy without and with zero-point vibrational energy corrections

	Method	*r*(CO)	*r*(NiC)	*r*(*Ng*Ni)	BE_e	BE_0
NiCO	CASSCF	1.143	1.668	–	–	–
	MR-SDCI(+Q)	1.159	1.650	–	–	–
	CCSD(T)	1.162	1.642	–	–	–
He–NiCO	CCSD(T)	1.160	1.660	1.745	24.98	21.25
Ne–NiCO	CCSD(T)	1.161	1.649	2.160	15.52	13.85
Ar–NiCO	CCSD(T)	1.161	1.658	2.290	39.96	38.24

combine with a binding energy of 39.96 kJ/mol, which is reduced to 38.24 kJ/mol by including zero-point vibrational energy corrections. The Ar–Ni bond distance is evaluated as 2.290 Å. Due to the bonding of Ar and NiCO, the NiC bond length becomes longer by *ca.* 0.15 Å while the CO bond length is almost unchanged, indicating that the Ni–C bond becomes slightly weaker in Ar–NiCO. Interestingly the binding energy for Ne and NiCO (~15.52 kJ/mol) is weaker than that for He and NiCO (~24.98 kJ/mol).

Table 2 shows geometrical parameters of the equilibrium geometry of NiCO and *Ng*–NiCO (*Ng* = He, Ne, Ar, Kr, Xe) and the binding energy between *Ng* and NiCO determined by *B*3*LYP* and M*PWPW*91 methods. It is noted that these geometries are determined based on the counterpoise corrected interaction energy defined in Eq. (1). As to geometrical parameters for NiCO, the M*PWPW*91 values are in good agreement with the MR-SDCI(+Q) and CCSD(T) values in spite

Table 2. Equilibrium bond lengths (in Å) for NiCO and *Ng*–NiCO (*Ng* = He, Ne, Ar, Kr, Xe) and the binding energies (in kJ/mol) for *Ng*–NiCO including zero-point vibrational energy corrections and counterpoise (CP) corrections, calculated by *B*3*LYP* and M*PWPW*91 methods

	r(CO)	*r*(NiC)	*r*(*Ng*Ni)	BE_e	BE_0	BE_e^{cp}	BE_0^{cp}
*B*3*LYP*							
NiCO	1.149	1.663	–	–	–	–	–
He–NiCO	1.147	1.678	1.744	21.30	20.17	16.44	15.31
Ne–NiCO	1.149	1.666	2.225	9.79	8.58	7.78	6.57
Ar–NiCO	1.149	1.676	2.314	30.04	28.53	27.82	26.28
Kr–NiCO	1.149	1.680	2.415	36.86	35.31	34.94	33.39
Xe–NiCO	1.149	1.685	2.549	45.19	43.76	43.56	42.13
M*PWPW*91							
NiCO	1.164	1.654	–	–	–	–	–
He–NiCO	1.163	1.668	1.778	16.40	15.19	11.97	10.75
Ne–NiCO	1.164	1.657	2.274	7.70	6.53	5.90	4.73
Ar–NiCO	1.164	1.670	2.296	31.63	30.00	29.41	27.74
Kr–NiCO	1.164	1.675	2.391	40.96	39.25	39.08	37.36
Xe–NiCO	1.164	1.681	2.521	52.30	50.75	50.71	49.16

of multi-configurational character in the electronic structure, while the *B*3*LYP* values are closer to the CASSCF ones. As to geometrical parameters for *Ng*–NiCO (Ng = He, Ne, Ar), the M*PWPW*91 results are in better agreement with the CCSD(T) results than the *B*3*LYP* results. The binding energy calculated by DFT methods is relatively smaller than the corresponding CCSD(T) value. By including BSSE and ZPE corrections, the binding energy between Ar and NiCO are evaluated as 26.28 and 27.74 kJ/mol at the *B*3*LYP* and M*PWPW*91 levels, respectively. These values are still larger than a typical *van der Waals* interaction energy, and it is possible that an argon atom can combine with NiCO in the low temperature condition. As shown in Table 2, the larger noble gas atoms combine with NiCO with a larger binding energy except for He–NiCO.

Both *ab initio* and DFT calculations show that the order of the binding energy between *Ng* and NiCO is BE(Ne–NiCO) < BE(He–NiCO). This result is against our common knowledge that the binding energy of He should be smaller than Ne in *van der Waals* complexes. To get insight into the bonding mechanism between *Ng* and NiCO, we investigated natural atomic orbital populations and net charges for NiCO and *Ng*–NiCO derived from natural population analyses for M*PWPW*91 results. The results are given in Table 3. In NiCO, part of electrons ($\sim$0.11) in Ni ($3d^9 4s^1$) is transferred to CO part (net charges for C and O are +0.35 and −0.46, respectively). Due to the binding of *Ng* and NiCO, part of electrons of *Ng* is transferred to 4s and 3d orbitals of Ni; net charges for He, Ne, Ar, Kr, and Xe are 0.06, 0.02, 0.09, 0.11, and 0.14, respectively. Such an electron transfer can

Table 3. Natural atomic orbital populations in valence orbitals and net charges (Q) for Ni–C–O and *Ng*–Ni–C–O (*Ng* = He, Ne, Ar, Kr, Xe) derived from natural population analyses for M*PWPW*91 results; the dipole moment μ (in Debye) is also given

	Ni			C					O					*Ng*[1]				μ
	4s	3d	$+Q$	2s	2p	3s	3p	$+Q$	2s	2p	3s	3p	$+Q$	s	p	d	$+Q$	
NiCO	0.63	9.26	0.11	1.31	2.28	0.03	0.02	0.35	1.71	4.71	0.01	0.03	−0.46	–	–	–	–	3.32
He–NiCO	0.66	9.30	0.04	1.32	2.26	0.03	0.02	0.37	1.71	4.71	0.01	0.03	−0.46	1.94	–	–	0.06	3.40
Ne–NiCO	0.66	9.26	0.08	1.31	2.28	0.03	0.02	0.36	1.71	4.71	0.01	0.03	−0.47	1.99	5.98	–	0.02	3.74
Ar–NiCO	0.68	9.31	0.01	1.32	2.26	0.03	0.02	0.37	1.71	4.72	0.03	0.01	−0.47	1.97	5.92	0.01	0.09	4.32
Kr–NiCO	0.68	9.33	−0.01	1.33	2.25	0.03	0.02	0.37	1.71	4.72	0.03	0.01	−0.47	1.97	5.90	0.01	0.11	4.57
Xe–NiCO	0.68	9.35	−0.04	1.33	2.25	0.03	0.02	0.37	1.71	4.72	0.01	0.03	−0.47	1.97	5.87	0.01	0.14	4.86

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[1] 1s for He; 2s and 2p for Ne; 3s, 3p, and 3d for Ar; 4s, 4p, and 4d for Kr; 5s, 5p, and 5d for Xe

Table 4. Harmonic frequencies (in cm^{-1}) for NiCO and *Ng*–NiCO (*Ng* = He, Ne, Ar, Kr, Xe) calculated by *B*3*LYP* and M*PWPW*91 methods; experimental fundamentals for NiCO in solid argon [13] are also given; values in parentheses denote relative intensities

	ν(CO)	ν(NiC)	ν(NiCO)	ν(*Ng*Ni)	ν(*Ng*–NiCO)
*B*3*LYP*					
NiCO	2080.3 (125)	596.8 (1)	361.1 (2.8)	–	–
He–NiCO	2087.8 (38)	579.2 (1)	404.4 (0.50)	470.8 (0.57)	133.4 (0.00)
Ne–NiCO	2080.2 (92)	596.6 (1)	391.2 (1.2)	146.1 (0.02)	64.7 (0.15)
Ar–NiCO	2078.8 (57)	583.5 (1)	402.5 (0.33)	176.1 (0.01)	65.4 (0.04)
Kr–NiCO	2076.8 (52)	578.5 (1)	398.4 (0.23)	148.1 (0.01)	58.1 (0.05)
Xe–NiCO	2073.7 (47)	571.2 (1)	391.1 (0.14)	137.5 (0.03)	51.4 (0.04)
M*PWPW*91					
NiCO	2011.0 (440)	611.6 (1)	361.1 (16)	–	–
He–NiCO	2015.0 (74)	595.0 (1)	402.6 (1.7)	422.2 (0.95)	124.3 (0.01)
Ne–NiCO	2010.1 (327)	609.9 (1)	387.5 (7.8)	125.9 (0.23)	59.6 (0.90)
Ar–NiCO	2008.2 (111)	594.5 (1)	403.5 (1.0)	181.7 (0.02)	64.0 (0.09)
Kr–NiCO	2006.0 (91)	588.7 (1)	399.2 (0.63)	156.2 (0.04)	56.1 (0.10)
Xe–NiCO	2002.7 (73)	580.3 (1)	390.7 (0.35)	146.5 (0.08)	48.0 (0.07)
Exp	1994.5 (196)	591.1 (1)	409.1 (2)		

be invoked by the low-lying 3d and 4s vacant orbitals of Ni. The order in number of transferred electrons coincides with the order of the binding energy for *Ng* and NiCO. Atomic orbital populations for CO part in *Ng*–NiCO are almost unchanged from those in NiCO. The dipole moment in *Ng*–NiCO increases in the order of atomic number of Ng.

Table 4 shows harmonic frequencies and relative intensities for NiCO and *Ng*–NiCO (*Ng* = He, Ne, Ar, Kr, Xe) calculated by the *B*3*LYP* and M*PWPW*91 methods, with the experimental fundamentals of NiCO determined in solid argon [13]. The calculated frequencies were derived from the counterpoise corrected Hessian matrix in the same way as geometry optimization [35]. The frequencies, ν(CO), ν(NiC), and ν(*Ng*Ni), correspond to C–O, Ni–C, and *Ng*–Ni stretching modes, respectively, while ν(NiCO) and ν(*Ng*–NiCO) correspond to Ni–C–O and *Ng*–Ni–C–O bending modes, respectively. The Ni–C–O bending mode consists of bending motion of Ni–C–O fragment, while the *Ng*–Ni–C–O bending mode consists of rotational motion of NiCO relative to *Ng*. Since Ar–NiCO has a considerable binding energy as discussed above, there is a possibility that experimental frequencies are attributed not to NiCO but to Ar–NiCO. The comparison of the frequencies of Ar–NiCO with those of NiCO shows that the Ni–C–O bending frequency is largely shifted (increase of *ca.* 40 cm^{-1} (10%)) in both *B*3*LYP* and M*PWPW*91 results, while changes in the frequencies of Ni–C and C–O stretching modes are relatively small. The calculated frequencies of ν(NiCO) are 361.1 cm^{-1} (NiCO) and 402.5 cm^{-1} (Ar–NiCO) in *B*3*LYP* method, and 361.1 cm^{-1} (NiCO) and 403.5 cm^{-1} (Ar–NiCO) in M*PWPW*91 method. The experimental frequency was reported as 409.1 cm^{-1} [13] which is much closer to the calculated value for Ar–NiCO. The relative intensity is more sensitive to the

Table 5. Reduced masses (in amu) and force constants (in mdyne/Å) of the respective normal modes of NiCO and Ar–NiCO, calculated at the M*PWPW*91 level

NiCO	ν(CO)	ν(NiC)	ν(NiCO)
Reduced mass	13.223	19.021	12.925
Force constant	31.505	4.192	0.993

Ar–NiCO	ν(CO)	ν(NiC)	ν(NiCO)	ν(ArNi)	ν(Ar–NiCO)
Reduced mass	13.234	19.021	13.081	35.427	30.235
Force constant	31.444	3.961	1.255	0.689	0.073

functionals employed. Since M*PWPW*91 results are in better agreement with MR-SDCI(+Q) results in geometrical parameters, we compare the M*PWPW*91 results with the experimental ones. The relative intensities to ν(NiC) were evaluated as 440 and 16 for ν(CO) and ν(NiCO), respectively, for NiCO while the corresponding values are 111 and 1.0 for Ar–NiCO in M*PWPW*91 results. The corresponding experimental intensities are 196 and 2, which are much closer to calculated values for Ar–NiCO.

Table 5 shows reduced masses and force constants of the respective normal modes of NiCO and Ar–NiCO, determined by the M*PWPW*91 method. In each normal mode, the reduced mass in Ar–NiCO increases slightly compared to that in NiCO, which works to reduce the frequency. On the other hand, the force constant for ν(NiCO) increases largely from 0.993 to 1.255 mdyne/Å; this change can be related to the movement of each atom in the ν(NiCO) mode where an Ar–Ni bond distance increases. The effect of force constants is greater than the effect of reduced masses, resulting in increase of frequencies of ν(NiCO).

In the review on transition metal carbonyl complexes, 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" [17]. This description means that the DFT method has a tendency to underestimate the harmonic frequency. As is shown in Table 4, the M*PWPW*91 harmonic frequencies for Ar–NiCO are in good agreement with the experimental fundamentals for NiCO. Taking into account this agreement, we carried out normal mode analyses for the various isotopic species of NiCO (^{60}Ni^{12}C^{16}O, ^{58}Ni^{13}C^{16}O, ^{58}Ni^{12}C^{18}O, ^{58}Ni^{13}C^{18}O) and Ar–NiCO (^{40}Ar–^{60}Ni^{12}C^{16}O, ^{40}Ar–^{58}Ni^{13}C^{16}O, ^{40}Ar–^{58}Ni^{12}C^{18}O, ^{40}Ar–^{58}Ni^{13}C^{18}O) by the M*PWPW*91 method, and compared the respective isotopic shifts with the corresponding experimental values reported by *Joly* and *Manceron* [13]. Table 6 shows the results of this comparison. As is clearly shown in this table, isotopic shifts in Ar–NiCO are in better agreement with the corresponding experimental values, respectively, than those in NiCO. These results support that the experimental values in Ref. [13] are attributed to those of Ar–NiCO.

Ng–NiN$_2$

The NiN$_2$ molecule has an isovalent electronic configuration with NiCO, and the term of their ground state is $^1\Sigma^+$ with no degeneracy, which originates from the

Table 6. Isotopic shifts (in cm^{-1}) of M*PWPW*91 harmonic frequencies for the various isotopomers of NiCO and Ar–NiCO; experimental isotopic shifts for fundamentals of NiCO in solid argon [13] are also given

	ν(CO)	ν(NiC)	ν(NiCO)	ν(ArNi)	ν(Ar–NiCO)
$^{60}Ni^{12}C^{16}O$	0.0	−3.3	−0.2		
Ar–$^{60}Ni^{12}C^{16}O$	0.0	−3.2	−0.4	−0.7	−0.5
Exp	–	−3.0	–	–	–
$^{58}Ni^{12}C^{18}O$	−40.9	−16.3	−4.0		
Ar–$^{58}Ni^{12}C^{18}O$	−41.4	−15.5	−3.6	−0.7	−1.1
Exp	−41.0	−15.4	−3.7	–	–
$^{58}Ni^{13}C^{16}O$	−49.7	−5.7	−10.9		
Ar–$^{58}Ni^{13}C^{16}O$	−49.3	−5.6	−12.4	−0.3	−0.0
Exp	−47.9	−5.5	−12.7	–	–
$^{58}Ni^{13}C^{18}O$	−91.1	−21.1	−15.1	−15.1	
Ar–$^{58}Ni^{13}C^{18}O$	−92.1	−20.4	−16.1	−1.0	−1.1
Exp	−90.4	−20.2	−16.3	–	–

excited state of Ni, ^1D with $3d^94s^1$. The electronic structure of NiN_2 ($X\ ^1\Sigma^+$) was analyzed in detail previously [37–40]. Experimentally, following the initial studies by *Burdett* and *Turner* [41], *Huber et al.* [42, 43] studied the NN and NiN stretching vibrations of NiN_2 by matrix isolation infrared and *Raman* spectroscopy. Recently, *Manceron*, *Alikhani*, and *Joly* [14] reinvestigated the infrared spectrum of NiN_2 isolated in solid argon at low temperature, and determined all the metal-ligand vibrations. They also carried out DFT calculations to determine geometries and frequencies of NiN_2, and made the correspondence between experimental and theoretical frequencies on the assumption that the effect of argon matrix should not be so significant.

We have verified that the dominant electronic configuration in $X\ ^1\Sigma^+$ of NiN_2 is a closed-shell configuration, and that the weight of this dominant configuration was 77 and 71% in the CASSCF and MR-SDCI calculations, respectively. The corresponding weights for the ground state of NiCO are 84 (CASSCF) and 78% (MR-SDCI), respectively, and thus, NiN_2 has a more multiconfigurational character than NiCO. The equilibrium Ni–N bond length for NiN_2 ($X\ ^1\Sigma^+$) determined by the MR-SDCI(+Q), CASPT2, and CCSD(T) methods are 1.663, 1.660, and 1.728 Å, respectively. The norm for the CCSD wavefunction gets a large value of 2.1 at the optimized structure, where the norm corresponds to the relative rate of the CCSD wavefunction to the reference *Hartree-Fock* wavefunction. Thus, CCSD(T) gives a poor description for the electronic structure of NiN_2. It is noted that the norm for CCSD wavefunction was evaluated as 1.3 for NiCO ($X\ ^1\Sigma^+$), and the calculated geometrical structures were in good agreement with the MR-SDCI(+Q) values.

Geometrical parameters of the equilibrium geometry of NiN_2 and *Ng*–NiN_2 (*Ng* = He, Ne, Ar) and binding energies for *Ng* and NiN_2 determined by MR-SDCI(+Q), CASPT2, and CCSD(T) methods are given in Table 7. MR-SDCI(+Q) was not applied to *Ng*–NiN_2 because of a huge computational cost. The Ar–Ni bond distance is evaluated as 2.235 Å at the CASPT2 level. Due to the bonding of

Table 7. Equilibrium bond lengths (in Å) for NiN_2 and Ng–NiN_2 (Ng = He, Ne, Ar) and the binding energy (BE_e in kJ/mol) between Ng and NiN_2, calculated by MR-SDCI(+Q), CASPT2, and CCSD(T) levels of theory

	Method	r(NN)	r(NiN)	r(NgNi)	BE_e
NiN_2	MR-SDCI(+Q)	1.126	1.663	–	–
	CASPT2	1.136	1.660	–	–
	CCSD(T)	1.120	1.728	–	–
He–NiN_2	CASPT2	1.133	1.677	1.687	30.84
	CCSD(T)	1.126	1.670	1.676	28.62
Ne–NiN_2	CASPT2	1.135	1.667	2.142	16.99
	CCSD(T)	1.127	1.661	2.121	14.23
Ar–NiN_2	CASPT2	1.135	1.673	2.235	48.20
	CCSD(T)	1.128	1.666	2.249	41.97

Ar and NiN_2, the NiN bond length becomes longer by *ca.* 0.013 Å while the NN bond length is almost unchanged, indicating that the Ni–N bond becomes slightly weaker in Ar–NiN_2. The binding energy for Ar–NiN_2 was evaluated as BE(CASPT2) = 48.20 and BE(CCSD(T)) = 41.97 kJ/mol. These results indicate that Ar–NiN_2 is more strongly bound than typical *van der Waals* complexes.

As is the case of Ar–NiN_2, both He and Ne combine with NiN_2, respectively, although their binding energies are relatively small compared to that of Ar–NiN_2. According to Table 7, Ng–Ni bond lengths in Ne–NiN_2 and He–NiN_2 are evaluated as 2.142 (Ne–Ni) and 1.687 Å (He–Ni), respectively, at the CASPT2 level. The tendency in changes of Ni–N and N–N bond lengths for He–NiN_2 is the same as that for Ar–NiN_2, *i.e.*, the Ni–N bond becomes slightly longer while the N–N bond is almost unchanged. On the other hand, in Ne–NiN_2 both Ni–N and N–N bond lengths are almost unchanged from those of NiN_2. The CASPT2 binding energies for Ne–NiN_2 and He–NiN_2 are evaluated as 16.99 and 30.84 kJ/mol, respectively, and thus, the binding in Ne–NiN_2 is relatively weaker than those in He–NiN_2 and Ar–NiN_2.

Table 8 shows geometrical parameters of the equilibrium geometry of NiN_2 and Ng–NiN_2 (Ng = He, Ne, Ar, Kr, Xe) and the binding energy between Ng and NiN_2 determined by *B*3*LYP* and M*PWPW*91 methods. These geometries are determined based on the counterpoise corrected interaction energy defined in Eq. (1). Through normal mode analyses it was verified that these Ng–NiN_2 compounds take a linear equilibrium structure. As to geometrical parameters DFT results are in good agreement with ab initio results in spite of multi-configurational character in the electronic structure. The M*PWPW*91 values are relatively better than the *B*3*LYP* values. The binding energy between Ar and NiN_2 are estimated as BE(*B*3*LYP*) = 36.90 and BE(M*PWPW*91) = 40.29 kJ/mol, which are relatively smaller than the CCSD(T) and CASPT2 values. By including both ZPE and CP corrections, the binding energy for Ar–NiN_2 is evaluated as 32.51 and 35.69 kJ/mol by *B*3*LYP* and M*PWPW*91 methods, respectively. Thus, these corrections do not change the result that Ar and NiN_2 combine with a larger binding energy than expected.

Table 8. Equilibrium bond lengths (in Å) for NiN_2 and *Ng*–NiN_2 (*Ng* = He, Ne, Ar, Kr, Xe) and the binding energies (in kJ/mol) for *Ng*–NiN_2 including zero-point vibrational energy corrections and counterpoise (CP) corrections, calculated by *B*3*LYP* and M*PWPW*91 methods

	r(NN)	*r*(NiN)	*r*(*Ng*Ni)	BE_e	BE_0	BE_e^{cp}	BE_0^{cp}
*B*3*LYP*							
NiN_2	1.111	1.686					
He–NiN_2	1.110	1.701	1.670	30.29	28.95	24.39	23.05
Ne–NiN_2	1.111	1.688	2.162	12.34	10.96	10.00	8.62
Ar–NiN_2	1.111	1.698	2.258	36.90	35.06	34.35	32.51
Kr–NiN_2	1.111	1.702	2.360	44.69	42.80	42.51	40.63
Xe–NiN_2	1.111	1.708	2.494	54.27	52.51	52.43	50.63
M*PWPW*91							
NiN_2	1.130	1.665					
He–NiN_2	1.128	1.679	1.696	25.19	23.77	19.66	18.28
Ne–NiN_2	1.130	1.668	2.201	10.25	8.91	8.08	6.74
Ar–NiN_2	1.129	1.680	2.240	40.29	38.28	37.66	35.69
Kr–NiN_2	1.129	1.685	2.338	51.13	49.04	48.91	46.82
Xe–NiN_2	1.129	1.692	2.470	64.39	62.43	62.51	60.58

Table 9 shows natural atomic orbital populations and net charges for Ni–$N^{(a)}$–$N^{(b)}$ and *Ng*–Ni–$N^{(a)}$–$N^{(b)}$ derived from natural population analyses for M*PWPW*91 results. In NiN_2, part of electrons (~0.22) in Ni ($3d^9 4s^1$) is transferred to N_2 part (0.16 in $N^{(a)}$ and 0.05 in $N^{(b)}$). Due to the binding of *Ng* and NiN_2, part of electrons of *Ng* is transferred to 4s and 3d orbitals of Ni (in $NeNiN_2$ the electron is transferred only to 4s); net charges for He, Ne, Ar, Kr, and Xe are 0.07, 0.03, 0.09, 0.12, and 0.15, respectively. Such an electron transfer can be invoked by the low-lying 3d and 4s vacant orbitals of Ni. The order in number of transferred electrons can be related to the order of the binding energy for *Ng* and NiN_2. The dipole moment in *Ng*–NiN_2 changes from that of NiN_2, which is caused by the electron transfer from *Ng* to Ni.

Table 10 shows harmonic frequencies and relative intensities for NiN_2 and *Ng*–NiN_2 (*Ng* = He, Ne, Ar, Kr, Xe) calculated by the *B*3*LYP* and M*PWPW*91 method, with the experimental fundamental frequencies of NiN_2 isolated in argon matrix [14]. The comparison of the frequencies of *Ng*–NiN_2 with those of NiN_2 shows that the Ni–N–N bending frequency is largely shifted (increase of *ca.* 50 cm^{-1} (16%) in Ar–NiN_2 and He–NiN_2), while changes in the frequencies of Ni–N and N–N stretching modes are relatively small. Table 11 shows reduced masses and force constants of the respective normal modes of NiN_2 and Ar–NiN_2 calculated by the M*PWPW*91 method. In each normal mode, the reduced mass in Ar–NiN_2 increases slightly (or is almost the same) compared to that in NiN_2, which works to reduce the frequency. On the other hand, the respective force constants for ν(NN) and ν(NiNN) in Ar–NiN_2 increase compared to those in NiN_2, which work to increase the frequency. It is noted that the force constant for ν(NiNN) increases largely from 0.802 to 1.097 mdyne/Å; this change can be related to the movement of each atom in the ν(NiNN) mode where an Ar–Ni bond distance increases. The effect of force

Table 9. Natural atomic orbital populations in valence orbitals and net charges (Q) for Ni–$N^{(a)}$–$N^{(b)}$ and Ng–Ni–$N^{(a)}$–$N^{(b)}$ (Ng = He, Ne, Ar, Kr, Xe) derived from natural population analyses for M*PWPW*91 results; the dipole moment μ (in Debye) is also given

	Ni			$N^{(a)}$				
	4s	3d	$+Q$	2s	2p	3s	3p	$+Q$
NiN_2	0.57	9.21	0.22	1.47	3.62	0.03	0.01	−0.16
He–NiN_2	0.61	9.26	0.13	1.47	3.63	0.03	0.01	−0.16
Ne–NiN_2	0.60	9.21	0.19	1.47	3.64	0.03	0.01	−0.16
Ar–NiN_2	0.62	9.26	0.12	1.47	3.63	0.03	0.01	−0.15
Kr–NiN_2	0.62	9.28	0.10	1.47	3.62	0.03	0.01	−0.15
Xe–NiN_2	0.61	9.31	0.07	1.48	3.62	0.04	0.02	−0.16

	$N^{(b)}$					Ng^1				μ
	2s	2p	3s	3p	$+Q$	s	p	d	$+Q$	
NiN_2	1.61	3.39	0.02	0.01	−0.05	–	–	–	–	3.16
He–NiN_2	1.61	3.38	0.02	0.01	−0.13	1.93	–	–	0.07	3.11
Ne–NiN_2	1.61	3.40	0.02	0.01	−0.06	1.99	5.98	–	0.03	3.62
Ar–NiN_2	1.61	3.40	0.02	0.01	−0.06	1.97	5.92	0.02	0.09	4.13
Kr–NiN_2	1.61	3.40	0.02	0.01	−0.06	1.97	5.89	0.01	0.12	4.35
Xe–NiN_2	1.61	3.40	0.02	0.01	−0.06	1.97	5.86	0.02	0.15	4.59

[1] 1s for He; 2s and 2p for Ne; 3s, 3p, and 3d for Ar; 4s, 4p, and 4d for Kr; 5s, 5p, and 5d for Xe

Table 10. Harmonic frequencies (in cm^{-1}) for NiN_2 and Ng–NiN_2 (Ng = He, Ne, Ar, Kr, Xe) at the *B*3*LYP* and M*PWPW*91 level; experimental fundamental frequencies for NiN_2 isolated in solid argon [14] are also given; values in parentheses denote relative intensities

	ν(NN)	ν(NiN)	ν(NiNN)	ν(NgNi)	ν(Ng–NiN_2)
*B*3*LYP*					
NiN_2	2253.8 (27)	559.7 (1)	301.4 (0.54)		
He–NiN_2	2268.1 (10)	579.3 (1)	349.0 (0.10)	533.7 (0.28)	162.0 (0.02)
Ne–NiN_2	2256.2 (22)	560.6 (1)	333.9 (0.23)	167.9 (0.01)	78.2 (0.01)
Ar–NiN_2	2257.3 (17)	547.7 (1)	343.2 (0.06)	197.8 (0.01)	77.2 (0.00)
Kr–NiN_2	2255.9 (17)	542.5 (1)	338.0 (0.04)	165.2 (0.01)	69.2 (0.01)
Xe–NiN_2	2253.9 (16)	534.3 (1)	329.6 (0.02)	152.9 (0.02)	62.4 (0.00)
M*PWPW*91					
NiN_2	2137.5 (26)	595.5 (1)	308.5 (2.2)		
He–NiN_2	2149.0 (14)	581.6 (1)	356.6 (0.26)	526.2 (0.31)	150.7 (0.02)
Ne–NiN_2	2138.9 (49)	595.3 (1)	340.4 (1.0)	150.9 (0.05)	72.4 (0.12)
Ar–NiN_2	2141.7 (28)	578.9 (1)	354.8 (0.18)	205.5 (0.03)	75.0 (0.02)
Kr–NiN_2	2140.8 (25)	572.4 (1)	349.0 (0.11)	174.6 (0.04)	66.7 (0.03)
Xe–NiN_2	2139.4 (22)	562.6 (1)	339.0 (0.06)	163.6 (0.06)	59.2 (0.02)
Exp	2089.5 (28)	563.5 (1)	357.0 (0.1)		

Table 11. Reduced masses (in amu) and force constants (in mdyne/Å) of the respective normal modes of NiN_2 and Ar–NiN_2, calculated at the M*PWPW*91 level

NiN_2	ν(NN)	ν(NiN)	ν(NiNN)		
Reduced mass	14.011	18.586	14.311		
Force constant	37.717	3.883	0.802		
Ar–NiN_2	**ν(NN)**	**ν(NiN)**	**ν(NiNN)**	**ν(ArNi)**	**ν(Ar–NiN_2)**
Reduced mass	14.008	18.791	14.791	34.802	27.149
Force constant	37.856	3.710	1.097	0.866	0.090

constants is greater than the effect of reduced masses in these two modes, resulting in increase of frequencies ν(NN) and ν(NiNN). According to changes in force constants, the NiN bond becomes slightly weaker while the NN bond becomes slightly stronger in Ar–NiN_2. This tendency in changes of frequencies between NiN_2 and *Ng*–NiN_2 coincide with the cases of NiCO and *Ng*–NiCO.

The experimental frequencies were those determined for NiN_2 isolated in solid argon [14]. Since Ar–NiN_2 has a considerable binding energy as discussed above, there is a possibility that these experimental frequencies are attributed not to NiN_2 but to Ar–NiN_2. The most distinguished change between NiN_2 and Ar–NiN_2 appears in the Ni–N–N bending frequency. As shown in Table 10, the experimental frequency for ν(NiNN) is 357.0 cm^{-1} which is very close to the corresponding M*PWPW*91 frequency, 354.8 cm^{-1}, for Ar–NiN_2; the corresponding M*PWPW*91 frequency for NiN_2 is 308.5 cm^{-1}. Table 10 also shows that the relative intensities calculated for Ar–NiN_2 (ν(NN):ν(NiN):ν(NiNN) = 28:1:0.18) are much closer to the experimental values (28:1:0.1) than the calculated values for NiN_2 (26:1:2.2). In Ar–NiN_2, there are additional vibrational modes of ν(ArNi) (~205.5 cm^{-1}) and ν(Ar–NiNN) (~75.0 cm^{-1}), but their intensity may be too small to be observed in the experimental spectrum.

Table 12 shows isotopic shifts of vibrational frequencies for NiN_2 ($^{60}Ni^{14}N^{14}N$, $^{58}Ni^{14}N^{15}N$, $^{60}Ni^{14}N^{15}N$, $^{58}Ni^{15}N^{14}N$, $^{60}Ni^{15}N^{14}N$, $^{58}Ni^{15}N^{15}N$, $^{60}Ni^{15}N^{15}N$) and Ar–NiN_2 (^{40}Ar–$^{60}Ni^{14}N^{14}N$, ^{40}Ar–$^{58}Ni^{14}N^{15}N$, ^{40}Ar–$^{60}Ni^{14}N^{15}N$, ^{40}Ar–$^{58}Ni^{15}N^{14}N$, ^{40}Ar–$^{60}Ni^{15}N^{14}N$, ^{40}Ar–$^{58}Ni^{15}N^{15}N$, ^{40}Ar–$^{60}Ni^{15}N^{15}N$) by the M*PWPW*91 method with the corresponding experimental values [14]. As is clearly shown, isotopic shifts in Ar–NiN_2 are in better agreement with the corresponding experimental values, respectively, than those in NiN_2. These results also support that the experimental frequencies in Ref. [14] are attributed to those of Ar–NiN_2.

Ng–CoCO

The vibrational frequencies of CoCO molecule have been reported by *Zhou* and *Andrews* [44, 45], and by *Tremblay et al.* [15], both of which have been determined by noble gas matrix isolation technique. *Tremblay et al.* reported all the fundamental frequencies of CoCO and several isotopomers determined in solid argon [15]. Theoretically all previous calculations on CoCO were carried out by several

Table 12. Isotopic shifts (in cm^{-1}) of M*PWPW*91 harmonic frequencies for the various isotopomers of NiN_2 and Ar–NiN_2; experimental isotopic shifts for fundamentals of NiN_2 in solid argon [14] are also given

NiN_2	ν(NN)	ν(NiN)	ν(NiNN)	ν(ArNi)	ν(Ar–NiN_2)
$^{60}Ni^{14}N^{14}N$	0.0	−3.2	−0.2		
Ar–$^{60}Ni^{14}N^{14}N$	0.0	−3.2	−0.4	−0.7	−0.6
Exp	–	−3.1	–		
$^{58}Ni^{14}N^{15}N$	−33.0	−7.7	−2.6		
Ar–$^{58}Ni^{14}N^{15}N$	−33.3	−7.3	−2.2	−0.4	−0.8
Exp	−32.5	−6.8	−2.6		
$^{60}Ni^{14}N^{15}N$	−33.0	−11.0	−2.8		
Ar–$^{60}Ni^{14}N^{15}N$	−33.3	−10.6	−2.6	−1.1	−1.4
Exp	–	−10.0	–		
$^{58}Ni^{15}N^{14}N$	−38.5	−6.2	−7.4		
Ar–$^{58}Ni^{15}N^{14}N$	−38.3	−6.0	−8.8	−0.4	−0.0
Exp	−36.5	−5.5	−8.8		
$^{60}Ni^{15}N^{14}N$	−38.5	−9.5	−7.6		
Ar–$^{60}Ni^{15}N^{14}N$	−38.3	−9.3	−9.3	−1.1	−0.6
Exp	–	−8.5	–		
$^{58}Ni^{15}N^{15}N$	−72.2	−13.5	−10.1		
Ar–$^{58}Ni^{15}N^{15}N$	−72.4	−12.9	−11.1	−0.8	−0.8
Exp	−69.6	−12.1	−11.4		
$^{60}Ni^{15}N^{15}N$	−72.2	−16.8	−10.3		
Ar–$^{60}Ni^{15}N^{15}N$	−72.4	−16.2	−11.5	−1.5	−1.4
Exp	–	−15.3	–		

DFT methods [15, 18, 44–48] except by us [12]. The electronic ground state of CoCO is $^2\Delta$, which originates from the excited state of Co, ^{2}F with $3d^84s^1$. In SA-CASSCF calculations for $X\,^2\Delta$ 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 wavefunction 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 wavefunction to the reference *Hartree-Fock* wavefunction. 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 RCCSD wavefunction 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 for Ar and CoCO determined by CASPT2 and RCCSD(T) methods are given in Table 13. The equilibrium Co–C bond length for CoCO ($X\,^2\Delta$) determined by the CASPT2 and RCCSD(T) methods are 1.668 and 1.684 Å, respectively. The Ar–Co bond distance is evaluated as 2.340 and 2.351 Å at the CASPT2 and RCCSD(T) levels, respectively. Due to the bonding of Ar and

Table 13. Equilibrium bond lengths (in Å) for CoCO and Ar–CoCO and the binding energy (BE_e in kJ/mol) between Ar and CoCO, calculated by CASPT2 and RCCSD(T) methods

	Method	*r*(CO)	*r*(CoC)	*r*(ArCo)	BE_e
CoCO	CASPT2	1.171	1.668	–	–
	RCCSD(T)	1.162	1.684	–	–
Ar–CoCO	CASPT2	1.172	1.677	2.340	34.06
	RCCSD(T)	1.166	1.670	2.351	30.17

Table 14. Equilibrium bond lengths (in Å) for CoCO and *Ng*–CoCO (*Ng* = He, Ne, Ar, Kr, Xe) and the binding energies for *Ng*–CoCO including zero-point vibrational energy corrections and counterpoise (CP) corrections, calculated by M*PWPW*91 methods

	r(CO)	*r*(CoC)	*r*(*Ng*Co)	BE_e	BE_0	BE_e^{cp}	BE_0^{cp}
CoCO	1.167	1.666	–	–	–	–	–
He–CoCO	1.163	1.668	1.778	12.18	11.09	7.36	6.28
Ne–CoCO	1.164	1.657	2.274	5.61	4.56	3.77	2.72
Ar–CoCO	1.164	1.670	2.296	25.36	23.81	22.93	21.38
Kr–CoCO	1.164	1.675	2.391	33.68	32.09	31.51	29.92
Xe–CoCO	1.164	1.681	2.521	43.81	42.51	41.88	40.58

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 binding energy was evaluated as BE(CASPT2) = 34.06 and BE(RCCSD(T)) = 30.17 kJ/mol. These results 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 above, and for Ar–FeCO by *Zhou* and *Andrews* [49].

Table 14 shows geometrical parameters of the equilibrium geometry of CoCO and *Ng*–CoCO (*Ng* = He, Ne, Ar, Kr, Xe) and the binding energy between *Ng* and CoCO determined by the UM*PWPW*91 method. Present calculations verified that *Ng*–CoCO takes a linear equilibrium structure. The UM*PWPW*91 values are in good agreement with the corresponding CASPT2 values in spite of multi-configurational character in the electronic structure. This tendency is also seen in *Ng*–NiCO and *Ng*–NiN_2. The binding energy between Ar and CoCO was evaluated as 25.36 kJ/mol which was further reduced to 21.38 kJ/mol by including counterpoise and ZPE corrections. Therefore, these corrections do not change the result that Ar and CoCO combine with a larger binding energy than expected.

Table 15 shows natural atomic orbital populations and net charges for Co–C–O and Ar–Co–C–O derived from natural population analyses for UM*PWPW*91 results. In CoCO, part of electrons (~0.10) in Co ($3d^8 4s^1$) is transferred to 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 electrons (~0.09) of Ar is transferred to 3d orbitals of Co. Such an electron transfer can be invoked by the low-lying 3d orbitals of Co. Atomic orbital populations for CO part in Ar–CoCO are less

Table 15. Natural atomic orbital populations in valence orbitals and net charges (Q) for Co–C–O and *Ng*–Co–C–O (*Ng* = He, Ne, Ar, Kr, Xe) derived from natural population analyses for M*PWPW*91 results; the dipole moment μ (in Debye) is also given

	Co			C				
	4s	3d	+Q	2s	2p	3s	3p	$+Q$
CoCO	0.83	8.57	0.10	1.27	2.32	0.02	0.02	0.37
He–CoCO	0.80	8.15	0.04	1.29	2.30	0.02	0.02	0.37
Ne–CoCO	0.82	8.10	0.08	1.27	2.31	0.02	0.02	0.37
Ar–CoCO	0.82	8.15	0.02	1.29	2.30	0.02	0.02	0.36
Kr–CoCO	0.82	8.18	0.00	1.30	2.29	0.03	0.02	0.36
Xe–CoCO	0.81	8.20	−0.03	1.30	2.29	0.03	0.02	0.36

	O					*Ng*[1]				
	2s	2p	3s	3p	$+Q$	S	p	d	$+Q$	μ
CoCO	1.71	4.71	0.01	0.03	−0.47	–	–	–	–	3.26
He–CoCO	1.71	4.72	0.01	0.03	−0.46	1.94	–	–	0.06	3.63
Ne–CoCO	1.71	4.72	0.01	0.03	−0.47	1.99	5.98	–	0.03	3.82
Ar–CoCO	1.71	4.72	0.01	0.03	−0.47	1.98	5.92	0.01	0.09	4.57
Kr–CoCO	1.71	4.72	0.01	0.03	−0.47	1.97	5.90	0.01	0.11	4.85
Xe–CoCO	1.71	4.72	0.01	0.03	−0.47	1.97	5.87	0.01	0.14	5.18

[1] 1s for He; 2s and 2p for Ne; 3s, 3p, and 3d for Ar; 4s, 4p, and 4d for Kr; 5s, 5p, and 5d for Xe

Table 16. Harmonic frequencies (in cm^{-1}) for CoCO and *Ng*–CoCO (*Ng* = He, Ne, Ar, Kr, Xe), calculated at the UM*PWPW*91 level; experimental fundamentals for CoCO in solid argon [15] are also given; values in parentheses denote relative intensities

	ν(CO)	ν(CoC)	ν(CoCO)	ν(*Ng*Co)	ν(*Ng*–CoCO)
CoCO	1978.9 (72)	599.1 (1)	373.0 (1.5)	–	–
He–CoCO	1991.1 (94)	594.8 (1)	428.6 (1.7)	389.6 (0.76)	149.6 (0.11)
Ne–CoCO	1983.8 (210)	606.2 (1)	402.2 (3.6)	108.9 (0.27)	62.2 (0.49)
Ar–CoCO	1983.7 (173)	595.1 (1)	422.6 (1.4)	165.2 (0.00)	71.9 (0.13)
Kr–CoCO	1981.7 (151)	590.1 (1)	419.3 (1.0)	142.9 (0.01)	65.9 (0.17)
Xe–CoCO	1978.5 (125)	583.1 (1)	411.9 (0.6)	135.2 (0.05)	60.9 (0.13)
Exp	1957.5 (430)	579.2 (1)	424.9 (4)		

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 16 shows harmonic frequencies and relative intensities (in parenthesis) for CoCO and Ar–CoCO calculated by the UM*PWPW*91 method, with the experimental fundamental frequencies and intensities of CoCO isolated in argon matrix [15]. 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 comparison of the frequencies of Ar–CoCO with those of CoCO shows that the Co–C–O

Table 17. Reduced masses (in amu) and force constants (in mdyne/Å) of the respective normal modes of CoCO and Ar–CoCO, calculated at the UM*PWPW*91 level

CoCO	ν(CO)	ν(CoC)	ν(CoCO)
Reduced mass	13.243	18.941	12.922
Force constant	30.554	4.006	1.059

Ar–CoCO	ν(CO)	ν(CoC)	ν(CoCO)	ν(ArCo)	ν(Ar–CoCO)
Reduced mass	13.233	18.913	13.095	35.873	29.946
Force constant	30.678	3.946	1.378	0.577	0.091

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. Table 17 shows reduced masses and force constants of the respective normal modes of CoCO and Ar–CoCO calculated by the UM*PWPW*91 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 mdyne/Å (in Ar–CoCO), which works 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.

The experimental frequencies were those determined for CoCO isolated in solid argon [15]. 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 Ar–CoCO appears in the Co–C–O bending frequency. As shown in Table 16, the experimental frequency for ν(CoCO) is 424.9 cm^{-1} which is very close to the corresponding UM*PWPW*91 frequency, 422.9 cm^{-1}, for Ar–CoCO; the corresponding UM*PWPW*91 frequency for CoCO is 373.0 cm^{-1}. This result supports that the experimental spectrum should be attributed 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. The relative intensity for ν(CO) gets a large value through the binding with Ar and CoCO ($72 \rightarrow 173$) which approaches to the experimental value, 430. In Ar–CoCO, there are additional vibrational modes of ν(ArCo) ($\sim$167.6 cm^{-1}) and ν(Ar–CoCO) ($\sim$72.5 cm^{-1}), but their intensity may be too small to be observed in the experimental spectrum.

Table 18 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 UM*PWPW*91 method with the corresponding experimental values [15]. 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 that the experimental frequencies in Ref. [15] are attributed to those of Ar–CoCO.

Table 18. Isotopic shifts (in cm^{-1}) of UM*PWPW*91 harmonic frequencies for the various isotopomers of CoCO and Ar–CoCO, with the corresponding experimental values [15]

CoCO	ν(CO)	ν(CoC)	ν(CoCO)	ν(ArCo)	ν(Ar–CoCO)
$^{59}Co^{12}C^{18}O$	−41.0	−15.8	−4.2		
Ar–$^{59}Co^{12}C^{18}O$	−40.8	−15.7	−3.7	−0.6	−1.3
Exp	−40.1	−15.0	−3.7		
$^{59}Co^{13}C^{16}O$	−48.4	−5.7	−11.3		
Ar–$^{59}Co^{13}C^{16}O$	−48.8	−5.7	−13.1	−0.3	−0.0
Exp	−47.2	−5.3	−13.2		
$^{59}Co^{13}C^{18}O$	−90.8	−20.7	−15.6		
Ar–$^{59}Co^{13}C^{18}O$	−91.0	−20.6	−16.8	−0.9	−1.3
Exp	−88.5	−19.5	−17.0		

Conclusions

In the present paper, we have applied ab initio multireference MR-SDCI(+Q) and CASPT2 methods, CCSD(T) method, and DFT methods using *B*3*LYP* and M*PWPW*91 functionals to investigate geometrical structures and vibrational frequencies of *Ng*–NiCO, *Ng*–NiN_2, and *Ng*–CoCO (*Ng* = He, Ne, Ar, Kr, Xe). First we examined the applicability of DFT methods to the above compounds which have a multiconfigurational character in electronic structure. According to the weight of dominant electronic configuration, NiN_2 has the most multiconfigurational character, and the CCSD(T) method predicts a slightly larger bond length for Ni–N. Through binding with noble gas atom, the multiconfigurational character is weakened in all compounds. In spite of multiconfigurational character, both *B*3*LYP* and M*PWPW*91 methods can predict similar geometrical parameters to MR-SDCI(+Q) and CASPT2 results. As to the present system, M*PWPW*91 functional gives better results than *B*3*LYP* functional.

For the respective compounds, it is shown that the noble gas atoms can make a relatively stronger bond with the transition metal compounds, NiCO, NiN_2, and CoCO, respectively, than a typical *van der Waals* interaction energy. DFT methods predict a slightly smaller binding energy than *ab initio* methods. By including the zero-point vibrational energy and the counterpoise correction, the binding energy was evaluated as 27.74 (Ar–NiCO), 35.69 (Ar–NiN_2), and 21.38 kJ/mol (Ar–CoCO) at the M*PWPW*91 level. It was verified that the larger noble gas atoms combine with transition metal compounds with a larger binding energy except for He. To examine the binding mechanism between *Ng* and transition metal compounds, natural population analyses were carried out for the respective compounds. In all compounds, part of electrons ($\sim$0.1) is transferred to the low-lying 3d and 4s vacant orbitals of Ni or Co, resulting in a relatively strong binding.

Normal mode analyses show that the bending frequency of Ni–C–O, Ni–N–N, and Co–C–O increases through binding with noble gas atoms: from 361.1 (NiCO) to 403.5 cm^{-1} (Ar–NiCO); from 308.5 (NiN_2) to 354.8 cm^{-1} (Ar–NiN_2); from 373.0 (CoCO) to 422.6 cm^{-1} (Ar–CoCO), at the M*PWPW*91 level. The corresponding experimental frequencies determined in solid argon are 409.1 (NiCO), 357.0 (NiN_2), and 424.9 cm^{-1} (CoCO) [13–15]. These results indicate that the experimental frequencies should be attributed to those of Ar–NiCO, Ar–NiN_2, and Ar–CoCO, respectively. We also calculated the relative intensities for each mode and the isotopic shifts, and verified that the experimental values are much closer to the corresponding values calculated for Ar-compounds than those for NiCO, NiN_2, and CoCO, respectively. In conclusion, we propose that spectroscopic data of transition metal compounds determined with the noble gas matrix isolation technique should be reinvestigated more carefully, taking into account the possibility that the target molecule makes a compound with noble gas atoms.

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