Matrix Isolation Infrared Spectroscopic and Theoretical Study of NgMO (Ng = Ar, Kr, Xe; M = Cr, Mn, Fe, Co, Ni) Complexes

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The matrix isolation infrared spectroscopic and quantum chemical calculation results indicate that late transition metal monoxides CrO through NiO coordinate one noble gas atom in forming the NgMO complexes (Ng = Ar, Kr, Xe; M = Cr, Mn, Fe, Co, Ni) in solid noble gas matrixes. Hence, the late transition metal monoxides previously characterized in solid noble gas matrixes should be regarded as the NgMO complexes, which were predicted to be linear. The M−Ng bond distances decrease, while the M−Ng binding energies increase from NgCrO to NgNiO. In contrast, the early transition metal monoxides, ScO, TiO, and VO, are not able to form similar noble gas atom complexes.

Introduction

During the past 50 years, the matrix isolation technique has proved to be a valuable tool for spectroscopic study of free radicals and other transient chemical reaction intermediates.[1−4] It is generally assumed that the noble gas matrix that confines the transient species is electronically innocent; that is, the transient species trapped in the solid matrix can be regarded as isolated "gas-phase" molecules. This assumption is normally valid in lighter noble gas, neon and argon, matrixes. The ground-state fundamental vibrations for covalently bonded molecules trapped in solid neon or argon often are slightly shifted from the gas-phase band centers. Matrix shifts of most diatomic molecules isolated in solid argon are less than 2%, and shifts for the molecules isolated in neon are even smaller.[5] However, recent experimental and theoretical investigations indicate that this assumption breaks down for some transition metal as well as actinide metal compounds.[6−11] A large number of chemically bound complexes containing noble gas atoms, xenon, krypton, and even argon, have been prepared.[12−24] Matrix isolation infrared spectroscopic and quantum chemical studies indicated that actinide metal compounds such as CUO, UO_2^+, and UO_2 trapped in noble gas matrixes are coordinated by multiple noble gas atoms.[6−8] The CUO, UO_2, and UO_2^+ species observed in solid noble gas matrixes should be regarded as the $UO_2(Ng)_n$ and $[UO_2(Ng)_n]^+$ complexes instead of the isolated molecules. Subsequent studies in our laboratory showed that transition metal oxide cations, ScO^+ and YO^+, and VO_2 and VO_4 neutrals are also coordinated by one or more noble gas atoms in forming noble gas complexes, which involve direct bonding interactions between metal and noble gas atoms.[9,10]

In this paper, we report a combined matrix isolation infrared spectroscopic and quantum chemical study of the noble gas complexes of first row transition metal monoxides. We will show that late transition metal monoxides CrO through NiO coordinate one noble gas atom in forming the NgMO complexes (Ng = Ar, Kr, Xe), while early transition metal monoxides ScO, TiO, and VO cannot coordinate noble gas atoms. As the simplest transition metal oxides, the 3d transition metal monoxides play an important role in high-temperature chemistry[25] and astrophysics,[26] and have been the subject of extensive experimental and theoretical investigations.[27−35] Their ground states and spectroscopic constants are reliably established. The noble gas−3d transition metal monoxide complexes serve as a simple model for understanding the transition metal−noble gas bonding in the other more complicated transition metal systems.

Experimental and Computational Methods

The experimental setup for pulsed laser ablation and matrix isolation Fourier transform infrared (FTIR) spectroscopic investigation has been described in detail previously.[36] Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, and 8 ns pulse width) was focused onto the rotating metal, or metal oxide targets (Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, Ni_2O_3). The ablated species were co-deposited with noble gas or O_2/noble gas mixtures onto a CsI window cooled normally to 6 K by means of a closed-cycle helium refrigerator. In general, matrix samples were deposited for 1−2 h at a rate of approximately 4 mmol/h. The Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, and Ni_2O_3 targets were prepared by sintered metal oxide powders. The Kr/Ar, Xe/Ar, O_2/Kr/Ar, and O_2/Xe/Ar mixtures were prepared in a stainless steel vacuum line using standard manometric technique. Isotopic $^{18}O_2$ (ISOTEC, 99%) was used without further purification. Infrared spectra were recorded on a Bruker IFS 66 V/S spectrometer at 0.5 cm^{-1} resolution between 4000 and 400 cm^{-1} using a DTGS detector. After the infrared spectrum of the initial deposition had been recorded, the samples were warmed to the desired temperature, quickly recooled, and the spectrum was taken followed by repetition of these steps using higher temperatures.

Quantum chemical calculations were performed using the Gaussian 03 program.[37] The calculations were performed at the level of density functional theory (DFT) with the B3LYP method, where the Becke three-parameter hybrid functional and the Lee−Yang−Parr correlation functional were used.[38] The 6-311+G(3df) basis sets were used for the O, Ar, Kr, Cr, Mn, Fe, Co, and Ni atoms, and the DGDZVP basis set was used for the Xe atom.[39,40] The geometries were fully optimized. The harmonic vibrational frequencies were calculated with analytic second

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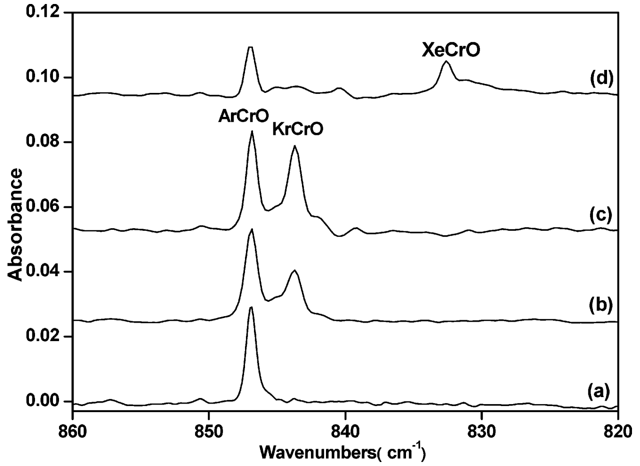

Figure 1. Infrared spectra in the 860−820 cm^{-1} region from co-deposition of laser-ablated chromium oxides with noble gases. (a) Pure Ar, 1 h of sample deposition at 6 K, (b) 2% Kr in Ar, 1 h of sample deposition at 6 K, (c) after annealing to 25 K, and (d) 1% Xe in Ar, 1 h of sample deposition at 6 K followed by 25 K annealing.

derivatives, and zero-point vibrational energies (ZPVE) were derived. The single-point energies of the structures optimized at the B3LYP/6-311+G(3df) level were calculated at the coupled cluster level with single and double excitations plus perturbative triple excitations (CCSD(T)) using the same basis sets.

Results and Discussion

The 3d transition metal monoxides can be prepared by two methods: laser ablation of bulk metal oxide targets, and reactions of laser-ablated metal atoms with dioxygen. Laser ablation of bulk Cr_2O_3, MnO_2, Fe_2O_3, Co_2O_3, and Ni_2O_3 metal targets produced the metal monoxides and dioxides as the major products. Co-condensation of laser-ablated metal atoms with oxygen in solid argon mainly produced metal−dioxygen species; the metal monoxide absorptions are weak, particularly for chromium, cobalt, and nickel. Therefore, the CrO, CoO, and NiO molecules were prepared only by laser ablation of bulk metal oxide targets, while both methods were employed to produce the MnO and FeO molecules. The 3d transition metal monoxides as well as other high oxide molecules have been trapped and identified in solid matrixes in previous studies.[41−46] To determine whether the oxide molecule trapped in solid argon is coordinated by noble gas atoms or not, and to determine the number of noble gas atoms that bind intimately to the oxide molecule, experiments were performed by using mixtures of a lighter noble gas host (Ar) doped with heavier noble gas guest atoms (krypton or xenon). Here, we focus only on the monoxides. The infrared spectra in the monoxide absorption regions with pure argon and krypton or xenon doped mixtures are shown in Figures 1−5for Cr, Mn, Fe, Co, and Ni, respectively.

NgCrO. The 846.3 cm^{-1} absorption in the spectra from co-deposition of laser-ablated chromium oxides with pure argon was previously assigned to the CrO molecule in solid argon.[41] As shown in Figure 1, a new absorption at 843.7 cm^{-1} was observed in the experiment with a 2% krypton-doped sample. This absorption increased on sample annealing at the expense of the 846.3 cm^{-1} absorption (Figure 1, trace c). Similarly, a new absorption at 832.6 cm^{-1} was produced on sample annealing when xenon was doped into the argon matrix (Figure 1, trace d). These experimental observations suggest that the 846.3 cm^{-1} absorption previously assigned to the isolated CrO molecule in solid argon should be reassigned to the ArCrO complex, and the 843.7 and 832.6 cm^{-1} absorptions in doped experiments are due to the KrCrO and XeCrO complexes, respectively. The KrCrO complex was observed at 834.1 cm^{-1} in solid krypton, while the XeCrO complex was observed at 821.1 cm^{-1} in solid xenon (Table 1).

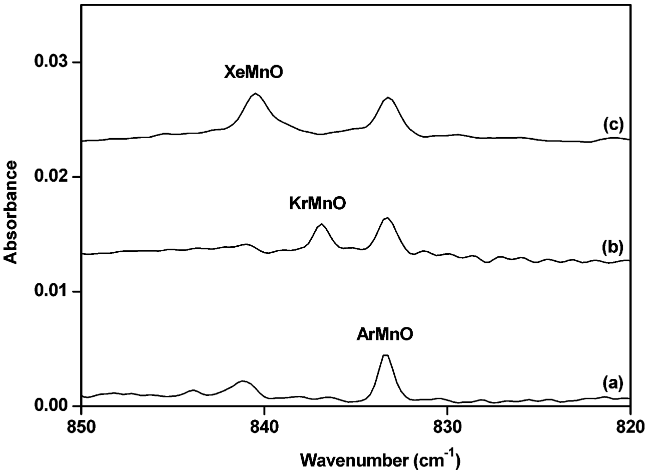

Figure 2. Infrared spectra in the 850−820 cm^{-1} region from co-deposition of laser-ablated manganese atoms with oxygen and noble gas mixtures. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing. (a) 0.5% O_2 in Ar, (b) 0.5% O_2 + 2% Kr in Ar, and (c) 0.5% O_2 + 3% Xe in Ar.

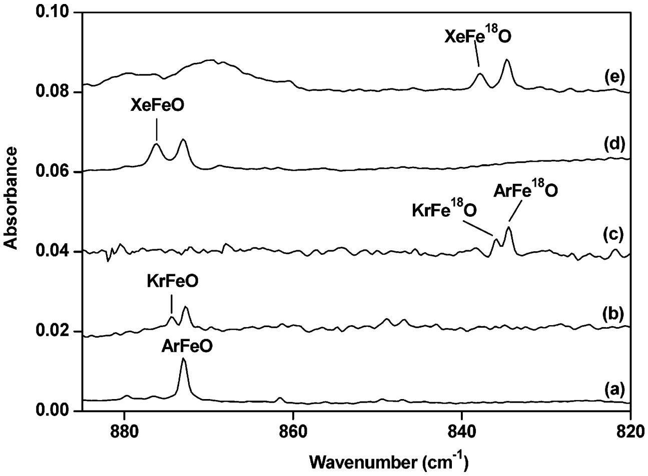

Figure 3. Infrared spectra in the 885−820 cm^{-1} region from co-deposition of laser-ablated iron atoms with oxygen and noble gas mixtures. Spectra were taken after 2 h of sample deposition at 6 K followed by 35 K annealing. (a) 0.5% $^{16}O_2$ in Ar, (b) 0.3% O_2 + 2% Kr in Ar, (c) 0.3% $^{18}O_2$ + 2% Kr in Ar, (d) 0.5% O_2 + 3% Xe in Ar, and (e) 0.5% $^{18}O_2$ + 1% Xe in Ar.

Theoretical calculations support the above assignment. The CrO molecule was predicted to have a $^5\Pi$ ground state, in agreement with the previous report.[32−35] The equilibrium Cr−O bond distance was computed to be 1.613 Å, very close to the experimental value of 1.615 Å.[28] Present DFT calculations also indicate that the CrO molecule is able to coordinate one argon atom in forming the ArCrO complex, which was predicted to have a $^5\Pi$ ground state with a linear structure. The Ar−Cr bond distance is evaluated as 3.300 Å at the B3LYP/6-311+G(3df) level. The Cr−O bond length elongates 0.004 Å upon Ar coordination. When the Ar atom is replaced by Kr and Xe in ArCrO, the Cr−O bond distances change to 1.621 and 1.625 Å, respectively. The harmonic vibrational fundamental of the $^5\Pi$ ground-state CrO was calculated to be 878.7 cm^{-1}, slightly lower than the experimentally determined gas-phase fundamental of 885.0 cm^{-1}.[47] The Cr−O stretching frequencies of the ArCrO,

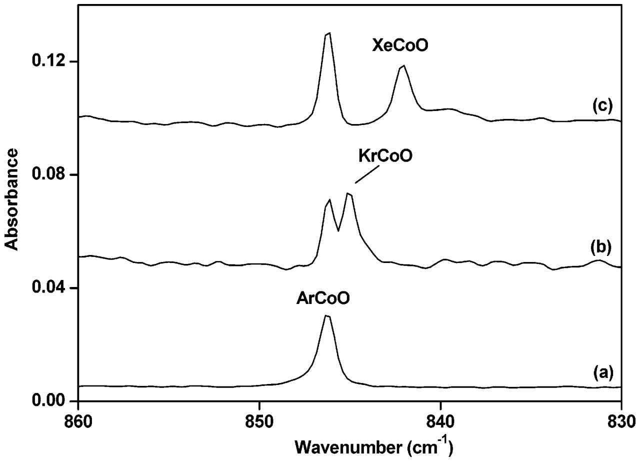

Figure 4. Infrared spectra in the 860−830 cm^{-1} region from co-deposition of laser-ablated cobalt oxides with noble gases. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing. (a) Pure Ar matrix, (b) 2% Kr in Ar, and (c) 2% Xe in Ar.

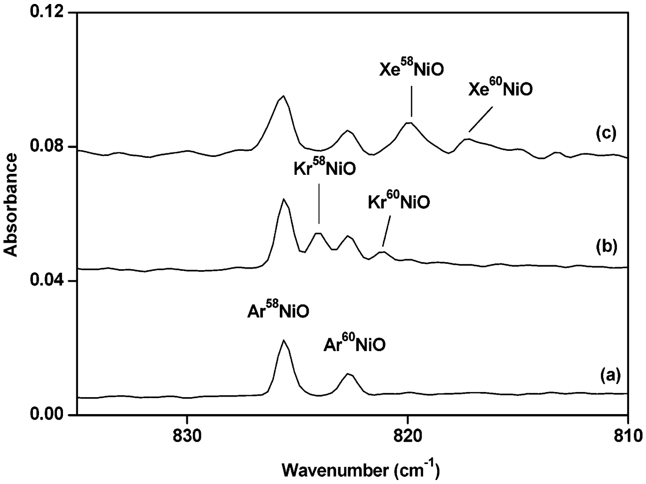

Figure 5. Infrared spectra in the 835−810 cm^{-1} region from co-deposition of laser-ablated nickel oxides with noble gases. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing. (a) Pure Ar matrix, (b) 2% Kr in Ar, and (c) 2% Xe in Ar.

KrCrO, and XeCrO complexes were computed at 864.9, 853.4, and 845.3 cm^{-1}, respectively.

NgMnO. The 833.1 cm^{-1} absorption in the Mn + O$_2$/Ar experiments was previously assigned to the MnO molecule isolated in solid argon based upon its oxygen isotopic shift and DFT theoretical frequency calculations.[42] When 2% Kr is doped into argon, a new absorption at 836.8 cm^{-1} was produced and increased on sample annealing during which the 833.1 cm^{-1} absorption decreased. A similar experiment with 3% xenon doped into argon exhibits another new absorption at 840.5 cm^{-1} (Figure 2). The experiment was repeated by using an isotopic labeled ^{18}O$_2$ sample. The 833.1 cm^{-1} band shifted to 796.7 cm^{-1} as reported previously,[42] while the 840.5 cm^{-1} absorption shifted to 803.9 cm^{-1}, which gave an ^{16}O/^{18}O isotopic ratio of 1.0455. This ratio is about the same as that of the 833.1 cm^{-1} band previously assigned to MnO (1.0457). The above-mentioned experimental observations suggest that the MnO molecule trapped in solid argon is coordinated by one argon atom. Hence, the 833.1 cm^{-1} band previously assigned to the isolated MnO molecule should be attributed to the ArMnO complex isolated in solid argon, and the 836.8 and 840.5 cm^{-1} absorptions that appeared in the doped experiments are due to the KrMnO and XeMnO complexes isolated in solid argon, respectively.

TABLE 1: Observed and Calculated (B3LYP) M−O Stretching Vibrational Frequencies of MO and NgMO (M = Cr, Mn, Fe, Co, Ni; Ng = Ar, Kr, Xe)

	gas	Ne[a]	Ar	Kr	Xe	calculated
CrO ($^5\Pi$)	885.0	880.2				878.7
ArCrO			846.3			864.9
KrCrO			843.7	834.1		853.4
XeCrO			832.6		821.1	845.3
MnO ($^6\Sigma^+$)	832.4					873.5
ArMnO			833.1			882.3
KrMnO			836.8	824.8		884.1
XeMnO			840.5		813.9	884.2
FeO ($^5\Delta$)	871.2					902.0
ArFeO			872.8			914.0
KrFeO			874.6	864.4		913.3
XeFeO			876.3		855.1	912.0
CoO ($^4\Delta$)	851.7	851.2				889.3
ArCoO			846.2			889.0
KrCoO			845.1	839.1		885.0
XeCoO			842.0		828.6	879.5
^{58}NiO ($^3\Sigma^-$)	828.3	831.4				861.1
Ar^{58}NiO			825.7			867.7
Ar^{60}NiO			822.8			864.5
Kr^{58}NiO			824.0	818.2		863.6
Kr^{60}NiO			820.1	815.3		860.5
Xe^{58}NiO			821.2		807.4	858.0
Xe^{60}NiO			817.2		804.9	853.7

[a] Neon values are from refs 55−57.

The NgMnO complexes were predicted to have a $^6\Sigma^+$ ground state with a linear structure, which correlates to the $^6\Sigma^+$ ground-state MnO.[32−35] The Ng−Mn bond distances were predicted to be 2.973, 2.987, and 3.089 Å, respectively, for ArMnO, KrMnO, and XeMnO. The Mn−O bond distances elongate from 1.635 Å in MnO to 1.638 Å in ArMnO, and to 1.639 and 1.642 Å when the Ar atom is replaced by Kr and Xe. The ground-state MnO was calculated to have a vibrational fundamental at 873.5 cm^{-1}. The calculated Mn−O stretching frequencies are blue-shifted about 8.8, 10.6, and 10.7 cm^{-1}, respectively, upon Ar, Kr, and Xe atom coordination. The experimental gas-phase fundamental of MnO was determined to be 840.0 cm^{-1}.[48] According to the calculation results, the gas-phase frequencies of NgMnO should be about 10 cm^{-1} higher than the MnO frequency.

NgFeO. In the Fe + O$_2$/Ar experiments, the band at 872.8 cm^{-1} corresponded to the absorption that was previously assigned to the FeO molecule isolated in solid argon.[43,44] In the experiments when krypton or xenon atoms were doped into argon, two distinct new absorptions were observed at 874.6 and 876.3 cm^{-1} (Figure 3). These two absorptions shifted to 836.0 and 837.9 cm^{-1} with the ^{18}O$_2$ sample. The resulting ^{16}O/^{18}O isotopic frequency ratios of 1.0462 and 1.0458 are about the same as that of the 872.8 cm^{-1} absorption and are characteristic of diatomic FeO stretching vibrations (the harmonic FeO diatomic ratio is 1.0462). These observations imply that the FeO molecules trapped in solid argon are not really “isolated” molecules and should be regarded as the ArFeO complex. Therefore, the 872.8 cm^{-1} absorption previously assigned to FeO is reassigned to the ArFeO complex isolated in solid argon, and the 874.6 and 876.3 cm^{-1} absorptions are attributed to the KrFeO and XeFeO complexes, resulting from the replacement of coordinated Ar atom by Kr and Xe atoms.

The FeO molecule has a $^5\Delta$ ground state with a bond length of 1.616 Å.[28] Its gas-phase vibrational fundamental was determined to be 871.3 cm^{-1}.[49] Present DFT/B3LYP calculations on the ground-state FeO gave a bond length of 1.611 Å and a harmonic vibrational frequency of 902.0 cm^{-1}, which are in quite good agreement with the experimental values. The NgFeO complexes were also predicted to have a $^5\Delta$ ground state with a linear

TABLE 2: Calculated (B3LYP/6-311+G(3df)) Geometric Structures (Bond Lengths in angstroms), Natural Atomic Charges, and M−Ng Binding Energies (kcal/mol) of MO and NgMO (M = Cr, Mn, Fe, Co, and Ni)

	$R_{\mathrm{M-O}}{}^{a}$	$R_{\mathrm{Ng-M}}$	q_{M}	q_{Ng}	$E_{\mathrm{b}}{}^{b}$	BSSE^{c}
CrO	1.613 (1.615)		0.77			
ArCrO	1.617	3.300	0.78	0.01	0.2 (1.3)	−0.2 (+0.9)
KrCrO	1.621	3.164	0.78	0.03	0.9 (2.1)	−0.2 (+0.9)
XeCrO	1.625	3.257	0.77	0.05	2.3 (3.1)	0.0 (+1.9)
MnO	1.635 (1.646)		0.82			
ArMnO	1.638	2.973	0.81	0.03	0.4 (1.3)	0.0 (+0.8)
KrMnO	1.639	2.987	0.80	0.04	1.1 (2.2)	+0.1 (+0.9)
XeMnO	1.642	3.089	0.79	0.06	2.0 (4.5)	+0.4 (+2.7)
FeO	1.611 (1.616)		0.82			
ArFeO	1.616	2.691	0.81	0.03	1.7 (1.7)	0.0 (+1.2)
KrFeO	1.617	2.779	0.80	0.04	2.8 (2.9)	0.0 (+1.2)
XeFeO	1.619	2.910	0.79	0.06	4.1 (6.0)	+0.6 (+4.3)
CoO	1.625 (1.629)		0.80			
ArCoO	1.634	2.561	0.76	0.06	2.8 (4.4)	−0.1 (+1.3)
KrCoO	1.636	2.623	0.76	0.08	4.1 (6.5)	+0.1 (+1.4)
XeCoO	1.639	2.784	0.73	0.11	5.7 (10.1)	+0.7 (+3.9)
NiO	1.626 (1.627)		0.74			
ArNiO	1.632	2.421	0.68	0.06	4.5 (7.2)	+0.1 (+1.4)
KrNiO	1.634	2.527	0.67	0.08	6.0 (9.2)	+0.2 (+1.5)
XeNiO	1.638	2.695	0.65	0.11	7.6 (13.1)	+0.6 (+3.5)

[a] Values in parentheses are experimental data from refs 28, 29, 47−51. [b] Binding energies without BSSE corrections. Values in parentheses are due to CCSD(T) calculations. Zero-point vibrational energies are included for the B3LYP values. [c] Basis set superposition error (BSSE) corrections. Values in parentheses are due to CCSD(T) calculations at the B3LYP optimized geometries.

structure. The predicted Fe−O stretching frequencies of NgFeO are blue-shifted when compared to that of free FeO (Table 1).

NgCoO. The 846.2 cm^{-1} absorption in the cobalt experiment is assigned to the ArCoO complex, and the new absorptions at 845.1 and 842.0 cm^{-1} observed in the experiments when Kr and Xe are doped are assigned to the KrCoO and XeCoO complexes, following the example of NgCrO, NgMnO, and NgFeO. The diatomic CoO molecule has a $^{4}\Delta$ ground state. Its vibrational fundamental was determined to be 851.7 cm^{-1} from laser-induced fluorescence study.[50] The Co−O stretching vibration of ArCoO was computed at 889.0 cm^{-1}. When the Ar atom is replaced by Kr and Xe in ArCoO, the Co−O stretching frequencies were predicted to be red-shifted by 4.0 and 9.5 cm^{-1}, respectively, slightly larger than the experimentally observed shifts of 1.1 and 4.2 cm^{-1}.

NgNiO. As shown in Figure 5, the absorptions at 825.7 and 822.8 cm^{-1} with intensity distribution of 2.5:1 were previously assigned to the ^{58}NiO and ^{60}NiO molecules.[44,46] When 2% krypton is doped into argon, two new absorptions at 824.0 and 820.1 cm^{-1} appeared and increased on sample annealing. The relative intensities between the 824.0 and 820.1 cm^{-1} absorptions also match the natural abundance of nickel. Similar absorptions at 821.2 and 817.2 cm^{-1} were observed in the xenon-doped experiment. The 825.7 and 822.8 cm^{-1} absorptions are reassigned to the Ar^{58}NiO and Ar^{60}NiO complexes isolated in solid argon, and the absorptions at 824.0, 820.1, 821.2, and 817.2 cm^{-1} are assigned to the Kr^{58}NiO, Kr^{60}NiO, Xe^{58}NiO, and Xe^{60}NiO complexes, respectively.

The NiO molecule has a $^{3}\Sigma$ ground state, and its vibrational frequency in the gas phase was determined to be 828.3 cm^{-1} (^{58}NiO).[51] The Ni−O stretching frequency of Ar^{58}NiO was computed at 867.7 cm^{-1}, blue-shifted by 6.6 cm^{-1} from the ^{58}NiO value calculated at the same level of theory (861.1 cm^{-1}). When the Ar atom in Ar^{58}NiO is replaced by Kr and Xe, the Ni−O stretching frequencies red-shifted by 4.1 and 9.7 cm^{-1}, respectively, which are slightly larger than the experimentally observed shifts of 1.7 and 4.5 cm^{-1}.

Calculations were also performed on the Ar$_2$MO complexes. Geometry optimization without symmetry constraint almost converged to ArMO + Ar, implying that MO can only coordinate one noble gas atom. As will be discussed, it involves bonding interaction between the coordinated noble gas atom and MO in the NgMO complexes. All of the other noble gas atoms in the matrix do not have bonding interaction with MO; they form the matrix cage to confine the NgMO complexes, which induces a red-shift of the M−O stretching frequency of the NgMO complexes. As listed in Table 1, the M−O stretching frequencies of the KrMO complexes in solid krypton are red-shifted by 6−12 cm^{-1} with respect to those in solid argon. The M−O stretching frequencies of XeMO in solid xenon are 12−27 cm^{-1} lower than those in solid argon.

In contrast to late transition metal monoxides, similar experiments on early transition metal monoxides, ScO, TiO, and VO, indicate that these monoxides trapped in solid argon do not form noble gas complexes.[9,10] Consistent with the experimental observations, quantum chemical calculations on ArScO, ArTiO, and ArVO almost converged to separated MO and Ar (with the M−Ar distances larger than 6 Å) with negligible binding energies, which indicated that ScO, TiO, and VO cannot form complexes with Ar.

Similar to the other previously characterized metal−noble gas complexes,[6−10] the bonding in the above characterized NgMO complexes also involves the Lewis acid−base interactions, in which electron density in the Ng lone pairs is donated into vacant orbitals of the metal center. Theoretical calculations indicated that the ground states of NgCrO, NgMnO, NgFeO, NgCoO, and NgNiO complexes are linear, which correlate to the ground states of metal monoxides. The ground states of CrO, MnO, FeO, CoO, and NiO have electron configurations of (core) $9\sigma^{1}4\pi^{1}1\delta^{2}$, (core) $9\sigma^{1}4\pi^{2}1\delta^{2}$, (core) $9\sigma^{1}4\pi^{2}1\delta^{3}$, (core) $9\sigma^{2}4\pi^{2}1\delta^{3}$, and (core) $9\sigma^{2}4\pi^{2}1\delta^{4}$, respectively. The 9σ and 1δ molecular orbitals are metal-based nonbonding orbitals. The doubly degenerated 4π molecular orbital is the antibonding combination of the metal 3dπ and O 2pπ atomic orbitals. The partially occupied 9σ and 4π molecular orbitals are the primary acceptor orbitals for donation from the noble gas atom. Consistent with the above notion, the calculated natural atomic charges for the metal centers decrease upon coordination of argon atom and upon replacement of argon by Kr and Xe, while the natural atomic charges of noble gas atoms are positive and increase from Ar to Xe, as listed in Table 2. The donation of electron density from the noble gas atom into the 4π antibonding orbital of MO weakens the M−O bond. As listed in Table 2, the calculated M−O bond distances increase monotonically upon Ar, Kr, and Xe atom coordination. The blue M−O stretching frequency shift when the M−O bond increases in the NgMnO and NgFeO complexes is likely due to the increased electrostatic interaction between Ng and MO.

The M−Ng binding energies for the above-characterized noble gas complexes calculated at the B3LYP and CCSD(T) levels of theory are listed in Table 2. The values calculated at the B3LYP level are systematically smaller than those calculated at the CCSD(T) level because of the lack of proper treatment for dispersive interactions with B3LYP. As can be seen in Table 2, the calculated M−Ng binding energies increase when Ar is replaced by Kr and Xe, and from chromium to nickel. This trend can be understood in that the 4π orbital energies of metal monoxides decrease from CrO to NiO, which favor the donation interaction between the metal monoxides and the noble gas atoms. For early transition metal monoxides, ScO, TiO, and VO, their 4π molecular orbitals are empty, but lie much higher in energy than the corresponding orbitals of the late transition metal monoxides, and thus the above-mentioned donation interactions are not observed between early transition metal monoxides and noble gas atoms.

The increasing binding energies from Ar to Xe suggest that heavier noble gas atoms can readily replace lighter noble gas atoms in the NgMO complexes, as experimentally observed. The binding energies of the ArCrO, ArMnO, and ArFeO complexes were predicted to be 2.2, 2.1, and 2.9 kcal/mol, respectively, at the CCSD(T)/B3LYP level of theory after basis set superposition error corrections. These binding energies are lower than those of the $(H_2)MO$, $(CH_4)MO$, and (NN)MO complexes, which have been characterized in the experiments when metal monoxides were co-deposited with H_2, CH_4, and N_2 in solid argon.[52−54] The $(H_2)MO$, $(CH_4)MO$, and (NN)MO complexes are formed via replacing the Ar atom in ArMO by the H_2, CH_4, and N_2 ligands in solid argon.

Conclusions

The combination of matrix isolation infrared spectroscopic and quantum chemical calculation results provides strong evidence that late 3d transition metal monoxides MO (M = Cr, Mn, Fe, Co, Ni) are coordinated by noble gas atoms in solid noble gas matrixes. The absorptions previously assigned to the MO molecules should be regarded as the ArMO complexes isolated in solid argon. The heavier Kr and Xe atoms can readily replace the Ar atom in ArMO to form the KrMO and XeMO complexes in the Kr- and Xe-doped experiments. The ground states of NgMO complexes were predicted to be linear and correlate to the ground states of the metal monoxides. The M−Ng bond distances decrease, while the M−Ng binding energies increase from NgCrO to NgNiO. The early transition metal monoxides, ScO, TiO, and VO, are not able to form similar noble gas atom complexes.

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