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Noble Gas−Transition Metal Complexes: Coordination of ScO^+ by Multiple Ar, Kr, and Xe Atoms in Noble Gas Matrixes

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The combination of matrix isolation infrared spectroscopic and density functional calculation results provides strong evidence that the transition metal monoxide cation, ScO^+, coordinates five noble gas atoms in forming the $[ScO(Ng)_5]^+$ (Ng = Ar, Kr, or Xe) complexes in noble gas matrixes.

During the past 50 years, the matrix isolation technique has proved to be a valuable tool for the spectroscopic study of free radicals and other transient chemical reaction intermediates.[1] 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. The ground state fundamental vibrations for most diatomic and small polyatomic molecules trapped in solid neon or argon matrixes only slightly shift from the gas phase band centers.[2] However, some molecules interact strongly with the noble gas matrixes. Many stable noble-gas-atom-containing species such as KrF_2, HXeCCH, HKrCCH, and HArF have been experimentally characterized.[3−6] Recent investigations have shown that the vibrational properties of CUO in an argon matrix are very different from those in a neon matrix. The experimental and theoretical results indicated the existence of direct bonding interactions between CUO and noble gas atoms in solid noble gas matrixes.[7] The binding of noble gas atoms to CUO causes a changeover in the electronic ground state of the $CUO(Ng)_n$ complexes.[8] Subsequent studies showed that other actinide compounds such as UO_2 and UO_2^+ trapped in noble gas matrixes are also coordinated by multiple noble gas atoms.[9,10]

The electronic and geometric structures of transition metal oxides have been widely studied.[11] Matrix isolation played an important role in determining the spectral and structural properties of transition metal oxide molecules.[12] We report that transition metal oxides also form a variety of noble gas complexes. Here, we show that the simplest transition metal oxide cation, ScO^+, trapped in solid noble gas matrixes, is coordinated by five noble gas atoms.

The laser-evaporation matrix isolation method used to prepare scandium oxides has been described in detail previously.[13] Briefly, the species from the laser evaporation of a bulk Sc_2O_3 target were co-deposited with Kr/Ar or Xe/Kr mixtures at 12 K. Infrared spectra were recorded following deposition and extensive annealing cycles using a Bruker IFS113V spectrometer at a 0.5 cm^{-1} resolution using a DTGS detector.

Co-deposition of laser-evaporated scandium oxides with pure argon at 12 K forms ScO as the major product with minor ScO^+ and ScO_2^- absorptions, which have previously been identified from the effects of isotopic substitution in their infrared spectra and theoretical calculations.[14,15] To determine the number of noble gas atoms that bind intimately to ScO^+ in the first coordination sphere, experiments were performed by using mixtures of a lighter noble gas host doped with heavier noble gas guest atoms. The infrared spectra for ScO^+ in pure argon and krypton and in mixtures of Kr/Ar are shown in Figure 1. Spectrum a shows the ScO^+ and ScO absorptions at 976.3 and 954.8 cm^{-1}, respectively, in pure argon, and spectrum f exhibits the ScO^+ and ScO absorptions at 965.3 and 949.6 cm^{-1}, respectively, in pure krypton. Spectra b−e illustrate the successive annealing cycles with a 3% Kr in argon sample. Five new absorptions at 974.4, 972.5, 970.6, 968.7, and 966.5 cm^{-1} appeared upon sample annealing to different temperatures. These absorptions lie between the ScO^+ absorptions in pure argon and the ScO^+ absorptions in pure krypton. Note that the intensities of the more red-shifted bands increased, whereas the higher

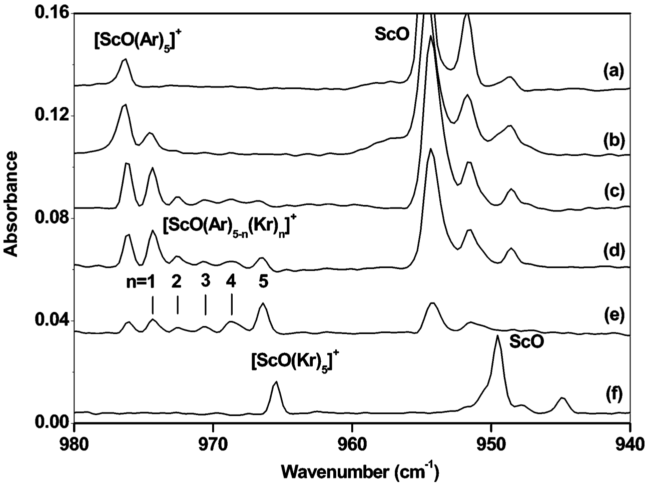

Figure 1. Infrared spectra in the 980−940 cm^{-1} region from the co-deposition of laser-evaporated scandium oxides with noble gases: (a) pure argon, after sample deposition at 12 K; (b) 3% Kr in argon, after deposition at 12 K; (c) after annealing to 35 K; (d) after annealing to 40 K; (e) after annealing to 45 K; (f) pure krypton, after sample deposition at 12 K.

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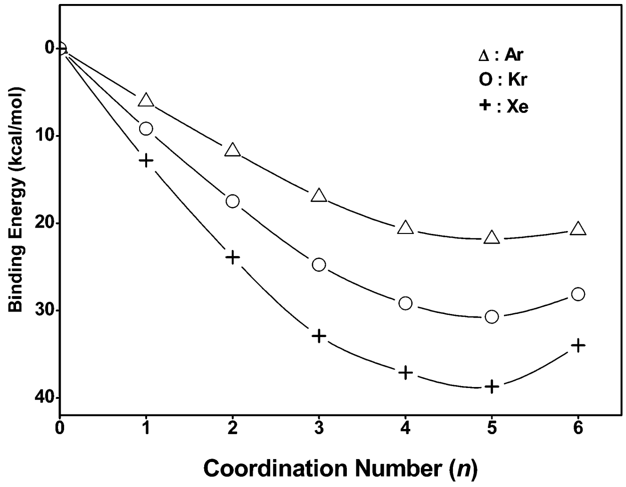

Figure 2. Total binding energy curves calculated for $[ScO(Ng)_n]^+$ (Ng = Ar, Kr, or Xe) complexes.

TABLE 1: Observed and Calculated Sc−O Stretching Frequencies (cm^{-1}) for $[ScO(Ng)_{5-n}(Ng')_n]^+$ in Solid Noble Gas Matrixes

		n					
Ng	Ng′	0	1	2	3	4	5
Ar	Kr	976.3	974.4	972.5	970.6	968.7	966.5
calcd		1039.9	1037.6	1035.0	1032.4	1030.3	1027.3
Kr	Xe	965.3	962.7	960.1	957.6	954.4	951.8
calcd		1027.3	1024.4	1021.8	1019.0	1016.8	1013.9

TABLE 2: Predicted Geometry Parameters (Å), Total Binding Energies (kcal/mol), and Sc−O Stretching Vibrational Frequencies (cm^{-1}) of ScO^+ and $[ScO(Ng)_5]^+$ (Ng = Ar, Kr, or Xe)

	Sc−O	Sc−Ng[a]	E_b	ν
ScO^+	1.612			1074.2
$[ScO(Ar)_5]^+$	1.632	2.839 (3.297)	21.8	1039.9
$[ScO(Kr)_5]^+$	1.639	2.979 (3.433)	30.7	1027.3
$[ScO(Xe)_5]^+$	1.645	3.197 (3.663)	38.7	1013.9

[a] The axial noble gas atom−Sc bond lengths are listed in parentheses.

bands of progressions decreased when the matrix sample was annealed to higher temperatures step by step. A similar experiment with 3% Xe in krypton produced a set of five new absorptions (Table 1) upon successive annealing cycles, which terminate around the pure xenon absorption at 952.1 cm^{-1}.

The above-mentioned experimental observations suggest that ScO^+ coordinates five noble gas atoms (Ng) in the first coordination sphere. The 976.3, 965.3, and 952.1 cm^{-1} absorptions in pure Ar, Kr, and Xe matrixes are due to $[ScO(Ng)_5]^+$ complexes isolated in solid matrixes, and the new band sets in experiments with mixtures of the noble gases are due to mixed $[ScO(Ar)_{5-n}(Kr)_n]^+$ and $[ScO(Kr)_{5-n}(Xe)_n]^+$ complexes (n = 1−5).

Quantum chemical calculations were performed for the $[ScO(Ng)_n]^+$ (Ng = Ar, Kr, or Xe; n = 0−6), $[ScO(Ar)_{5-n}(Kr)_n]^+$ (n = 1−5), and $[ScO(Kr)_{5-n}(Xe)_n]^+$ (n = 1−5) complexes using the Gaussian 03 program,[16] with the B3LYP functional[17] and 6-311+G(d) basis sets for oxygen, argon, krypton, and scandium atoms[18] and the SDD pseudopotential and basis set for xenon atoms.[19] The total binding energies for the $[ScO(Ng)_n]^+$ complexes are shown in Figure 2. We can see that the maximum total binding energy is achieved when $n = 5$. The $[ScO(Ng)_5]^+$ complexes have C_{4v} symmetry (Figure 3). The Sc−O stretching frequencies for $[ScO(Ng)_5]^+$ (Ng = Ar, Kr, or Xe) were predicted at 1039.9, 1027.3, and 1013.9 cm^{-1} (Table 2), respectively, in good agreement with the observed frequencies (976.3, 965.3, and 952.1 cm^{-1}). On the basis of the calculated frequency (1074.2 cm^{-1}), the yet-to-be-observed gas phase frequency for ScO^+ is suggested to be around 1012 cm^{-1}. Calculations on the $[ScO(Ar)_{5-n}(Kr)_n]^+$ complexes indicate that the total binding energy increases monotonically with increasing Kr substitution. The calculated Sc−O stretching frequencies of the $[ScO(Ar)_{5-n}(Kr)_n]^+$ series exhibit a monotonic red shift upon successive replacement of Ar atoms by Kr atoms (Table 1). Since the axial noble gas atom is slightly different from the equatorial atoms, the $[ScO(Ar)_{5-n}(Kr)_n]^+$ complexes (n = 1−4) may exist as structural isomers. Our calculations indicated that these structural isomers are very close in energy with a very small (0−0.5 cm^{-1}) Sc−O stretching frequency difference. We assume that the more strongly bound equatorial atoms were substituted prior to the axial atom. The calculated red shifts for successively substituting Ar atoms by Kr atoms of 2.3, 4.9, 7.5, 9.6, and 12.6 cm^{-1} are in good agreement with the experimentally determined shifts of 1.9, 3.8, 5.7, 7.6, and 9.8 cm^{-1}.

The interactions between noble gas atoms and ScO^+ in $[ScO(Ng)_n]^+$ involve the donation of a lone pair of noble gas atoms into empty, primarily Sc-based orbitals. The ScO^+ cation has a $^1\Sigma^+$ ground state with an electronic configuration of $(8\sigma)^2(3\pi)^4(9\sigma)^0(1\delta)^0$. The 9$\sigma$ LUMO is primarily a nonbonding hybrid of the Sc 4s and $3d_{z^2}$ orbitals that is directed away from the O atom. The 1δ LUMO+1 molecular orbital is largely the Sc 3d orbital that is mainly nonbonding. These orbitals are the primary acceptor orbitals for donation from the noble gas atoms. We found that HOMO-14 ($6b_2$) and HOMO-17 ($17a_1$) in $[ScO(Ar)_5]^+$ shown in Figure 3 are such bonding orbitals that involve donation from the filled Ar 3p orbitals onto the empty 9σ and 1δ orbitals of ScO^+. Since the 9σ and 1δ molecular orbitals of the $^2\Sigma^+$ ground state ScO lie much higher in energy than those of ScO^+, the above-mentioned donation interactions between ScO and noble gas atoms are not observed, and analogous complexes with ScO apparently do not form.

The present experiments show that Kr atoms readily replace Ar in the coordination sphere of ScO^+, and Xe replaces Kr.

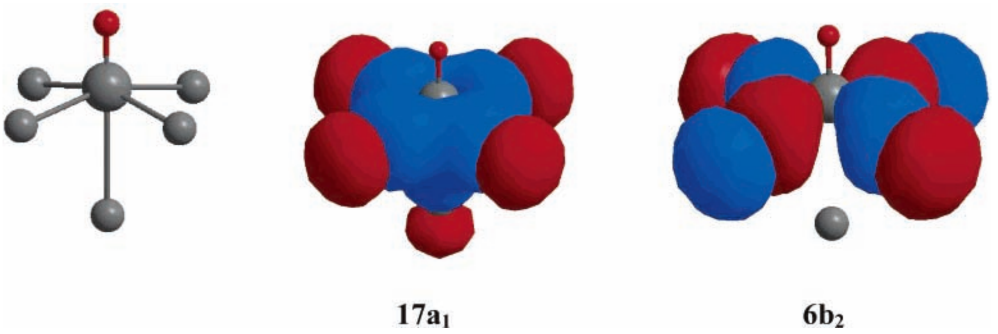

Figure 3. Optimized structure and molecular orbital pictures of the $[ScO(Ar)_5]^+$ complex.

The calculated binding energies for the $[ScO(Ng)_5]^+$ complexes are consistent with the experimental observations. The binding energies per Ng atom were computed to be 4.4, 6.4, and 7.7 kcal/mol for $[ScO(Ar)_5]^+$, $[ScO(Kr)_5]^+$, and $[ScO(Xe)_5]^+$, respectively. These computed binding energies are comparable to those calculated for UO_2^+ and those measured for transition metal carbonyl−noble gas complexes.[10,20,21]

In summary, the combination of experimental and theoretical results presented here provides strong evidence for multiple noble gas atom bonding to the transition metal center. The ScO^+ ion observed in solid matrixes should be regarded as the $[ScO(Ng)_5]^+$ complex. Experiments with dilute krypton in argon or xenon in krypton produced new IR bands, which are due to the stepwise formation of the $[ScO(Ar)_{5-n}(Kr)_n]^+$ and $[ScO(Kr)_{5-n}(Xe)_n]^+$ ($n = 1-5$) complexes. The experiments under investigation in our laboratory show that other transition metal oxide species such as transition metal dioxide neutrals also form a variety of noble gas complexes. These observations suggest that when large matrix shifts were observed, the formation of strong complexes with rare gas atoms should be considered.

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