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Coordination of niobium and tantalum oxides by Ar, Xe and O_2: Matrix isolation infrared spectroscopic and theoretical study of $NbO_2(Ng)_2$ (Ng = Ar, Xe) and $MO_4(X)$ (M = Nb, Ta; X = Ar, Xe, O_2) in solid argon

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ABSTRACT

The combination of matrix isolation infrared spectroscopic and quantum chemical calculation results indicate that the NbO_2 molecule is coordinated by two noble gas atoms in forming the $NbO_2(Ng)_2$ (Ng = Ar, Xe) complexes in solid noble gas matrixes. In contrast, the TaO_2 molecule is not able to form similar noble gas complex. The niobium and tantalum dioxides further react with dioxygen to form the side-on bonded superoxo-dioxide complexes MO_4 (M = Nb, Ta), which are coordinated by one argon atom in solid argon matrix. The coordinated Ar atom in $MO_4(Ar)$ can be replaced by O_2 or Xe in forming the MO_6 and $MO_4(Xe)$ complexes. The results indicate that the NbO_2, NbO_4 and TaO_4 molecules trapped in solid noble gas matrixes should be regarded as the $NbO_2(Ng)_2$ and $MO_4(Ng)$ (Ng = Ar, Xe; M = Nb, Ta) complexes instead of "isolated" metal oxide species.

1. Introduction

The electronic and geometric structures of transition metal oxides are of great chemical interest. The matrix isolation technique played an important role in providing valuable spectral and structural properties of transition metal oxide molecules. Recent investigations have shown that some metal oxides trapped in solid noble gas matrixes cannot be regarded as "isolated" species, they are coordinated by noble gas atoms in forming the noble gas complexes [1–6]. Matrix isolation infrared spectroscopic and quantum chemical studies indicate that actinide metal oxides such as UO_2^+ and UO_2 trapped in solid noble gas matrixes are coordinated by multiple noble gas atoms [1,2]. Subsequent studies in our laboratory showed that transition metal oxide cations and neutrals such as ScO^+, YO^+, MO (M = Cr–Ni), VO_2 and VO_4 are also coordinated by one or more noble gas atoms in forming the noble gas complexes, which involve direct bonding interactions between metal and noble gas atoms [3–6]. The noble gas atom coordination may lead to structural and vibrational frequency change for metal oxides with respect to those in the gas phase without noble gas atom coordination.

Niobium and tantalum oxides, similar to the oxides of their lighter homologue vanadium, are an interesting class of compounds with wide applications in catalysis, capacitor manufacture and high-temperature chemistry. Simple niobium and tantalum oxides such as monoxides and dioxides have received a great deal of attention [7–11]. The niobium and tantalum monoxides have been extensively studied spectroscopically in the gas phase as well as in solid matrixes, and the ground states as well as spectroscopic constants have been obtained [7–10]. Higher niobium and tantalum oxides and dioxygen complexes such as MO_2 and MO_4 have also been characterized from matrix isolation infrared spectroscopic study on the reaction of metal atoms with dioxygen in solid noble gas matrixes [11]. In the paper, we provide a joint matrix isolation infrared spectroscopic and theoretical study to show that some niobium and tantalum oxides including NbO_2, NbO_4 and TaO_4 are coordinated by noble gas atoms in forming noble gas complexes in solid noble gas matrixes, which involve direct bonding interaction between metal and noble gas atoms.

2. Experimental and computational methods

The experimental setup for pulsed laser-ablation and matrix isolation infrared spectroscopic investigation has been described in detail previously [12]. Briefly, the 1064 nm fundamental of a Nd:YAG laser (10 Hz repetition rate and 8 ns pulse width) was focused onto a rotating niobium or tantalum metal target (Johnson Matthey, 99.9%) through a hole in a CsI window cooled normally to 6 K by means of a closed-cycle helium refrigerator. The laser-evaporated metal atoms were co-deposited with oxygen and noble gas mixtures onto the CsI window. In general, matrix samples were deposited for 1–2 h at a rate of 3–5 mmol/h. The O_2/Ar and O_2/Xe/Ar mixtures were prepared in a stainless steel vacuum line using

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standard manometric technique. Isotopic $^{18}O_2$ (ISOTEC, 99%) were used without further purification. The infrared absorption spectra of the resulting sample were recorded on a Bruker IFS 66 V 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 up to a certain temperature, quickly recooled and more spectra were taken.

Quantum chemical calculations were performed using the Gaussian 03 program [13]. The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang and Parr (B3LYP) was utilized [14,15]. The 6-311+G(3df) basis set was used for O and Ar atoms [16,17], the DGDZVP basis set was used for Nb and Xe atoms [18,19] and SDD pseudo potential and basis set was used for Ta [20]. The geometries were fully optimized. In addition, the CCSD(T) method was also applied to calculate the single point energies of the B3LYP optimized structures with the same basis sets. The counterpoise method was applied to account for basis set superposition error (BSSE) in the calculation of the binding energy [21]. The harmonic vibrational frequencies were calculated at the B3LYP level and zero-point vibrational energies (ZPVE) were derived.

3. Results and discussion

Infrared spectra The reaction of laser-ablated niobium atoms with oxygen in solid argon has been investigated previously, and the oxide products have been identified from the effects of isotopic substitution in their infrared spectra and theoretical calculations [11]. We firstly repeated the experiment of laser-ablated niobium atoms with dioxygen reaction in solid argon. The spectra in the 1140–1100 and 970–860 cm^{-1} regions with a 0.5% O_2/Ar sample are shown in Fig. 1. The infrared spectra are about the same as that reported previously [11]. Besides the O_4^+ and O_4^- absorptions that are common for laser-ablated metal atom reactions with dioxygen [22], product absorptions at 933.5/931.1 and 875.9/869.8 cm^{-1} were observed after sample deposition at 6 K and increased upon 15 min of 250 < λ < 580 nm irradiation followed by 25 K annealing (trace b). These absorptions were previously assigned to the symmetric and antisymmetric ONbO stretching vibrations of the bent NbO_2 molecule at two trapping sites [11]. Subsequent sample annealing to 30 K produces a series of product absorptions at 1109.3, 945.9, 943.5, 903.6, 900.6 and 511.3 cm^{-1} at the expense of the NbO_2 absorptions (trace c). The 945.9 and 903.6 cm^{-1} absorptions decreased together while the 943.5 and 900.6 cm^{-1} increased together on sample annealing to 43 K (trace d). As has been mentioned [11], the 1109.3 and 511.3 cm^{-1} absorptions go together, although these two absorptions do not track with either pair of absorptions mentioned above, they track with the sum of 945.9 and 943.5 cm^{-1} and the 903.6 cm^{-1} absorption plus the 900.6 cm^{-1} absorption. These absorptions were previously assigned to the NbO_4 molecule with a (η^2-O_2)NbO_2 C_{2v} structure at different trapping sites [11].

Experiments were performed by using oxygen doped with Xe in excess argon. Fig. 2 shows the spectra in the 1120–1090 and 960–840 cm^{-1} regions from co-deposition of laser-ablated niobium atoms with 0.5% O_2 + 1.0% Xe in argon. After sample deposition, the same product absorptions presented in the experiment shown in Fig. 1 were observed. In addition, the $XeOO^+$ absorption was also observed [23]. As shown in Fig. 2, two groups of new absorptions at the low frequency side of the NbO_2 absorptions were evolved on sample annealing to high-temperatures. The 1109.3, 945.9, 903.6, and 511.3 cm^{-1} absorptions previously assigned to NbO_4 were produced as before. However, the 943.5 and 900.6 cm^{-1} absorptions were not formed on annealing. In contrast, a group of new absorptions at 1110.7, 940.6, 897.3 and 509.7 cm^{-1} increased markedly on sample annealing and dominated the spectrum after 40 K annealing. The product absorptions are listed in Table 1.

The spectra in the 1110–1090 and 970–860 cm^{-1} regions from co-deposition of laser-ablated tantalum atoms with dioxygen in excess argon are illustrated in Fig. 3, which are about the same as those reported previously. Besides the known O_4^- and O_4^+ species, weak absorptions at 965.3 and 906.9 cm^{-1} which were previously assigned to the symmetric and antisymmetric OTaO stretching vibrations of the bent TaO_2 molecule were observed after sample deposition [11]. When the sample was annealed to 25 K (trace b), product absorptions at 1095.7, 950.5, 894.5 and 524.2 cm^{-1} were produced at the expense of the TaO_2 absorptions. Another group of absorptions at 946.3, 889.4 and 522.4 cm^{-1} appeared when the sample was annealed to higher temperatures (traces c and d). These absorptions have been attributed to the TaO_4 molecule with a (η^2-O_2)$TaO_2$$C_{2v}$ structure at different matrix sites [11].

Similar experiments were also done with 0.5% O_2 in argon doped with 2.0% xenon. The infrared spectra in the 1110–1090

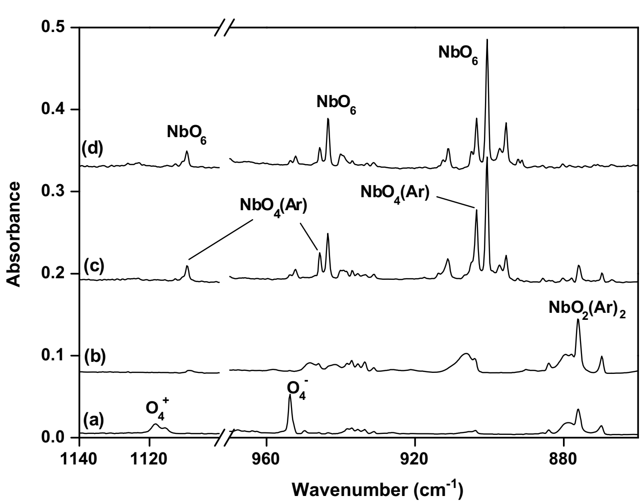

Fig. 1. The infrared spectra in the 1140–1100 and 970–860 cm^{-1} regions from co-deposition of laser-ablated niobium atoms with 0.5% O_2 in excess argon. (a) 1 h of sample deposition at 6 K, (b) after 15 min of 250 < λ < 580 nm irradiation followed by 25 K annealing, (c) after annealing to 30 K, and (d) after annealing to 43 K.

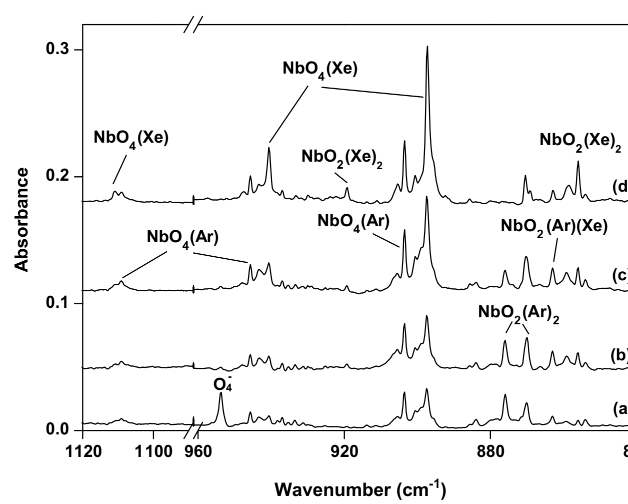

Fig. 2. The infrared spectra in the 1120–1090 and 960–840 cm^{-1} regions from co-deposition of laser-ablated niobium atoms with 0.5% O_2 + 1.0% Xe in argon. (a) 1.5 h of sample deposition at 6 K, (b) after 15 min of 250 < λ < 580 nm irradiation, (c) after annealing to 30 K, and (d) after annealing to 40 K.