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Reactions of Laser-Ablated Niobium and Tantalum Atoms with NO. Infrared Spectra of the NMO, M(η^1-NO)$_x$ (x = 2, 3), and (N_2)(MO_2) Molecules in Solid Argon

Mingfei Zhou and Lester Andrews*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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Laser-ablated Nb and Ta atoms react with NO to give primarily the NNbO and NTaO insertion products, which are identified from isotopic substitution and density functional calculations of isotopic frequencies. Although the mononitrosyls are not observed, annealing gives dinitrosyls the trinitrosyls for both metals. Photolysis markedly increases (N_2)(NbO_2) and (N_2)(TaO_2), which are stable end products for these reactions.

Introduction

There is increasing interest in understanding the chemistry of transition metals with ligands such as NO. A number of recent theoretical and experimental studies have addressed this topic. Density functional studies of first row transition metal mononitrosyl neutrals as well as cations have been reported.[1,2] Bonding of different [Fe, N, O] isomers have also been investigated.[3] Experimentally, iron, cobalt, nickel, and copper nitrosyls have been identified using matrix isolation spectroscopy.[4]

Recently, laser-ablated early first row transition metal atom reactions with NO molecules have been carried out in our laboratory.[5−7] Due to the high reactivity of laser-ablated metal atoms, insertion reactions to form NMO molecules were observed for the early metals, while addition reactions to form the nitrosyls MNO and cyclic M[NO] species proceeded on annealing in the argon matrix for all metals from Sc to Cu. However, there are no similar studies on the second and third row transition metals. It is interesting to know which behavior will dominate reactions of the second and third row metal atoms. Furthermore, the vanadium reaction with $(NO)_2$ gave evidence for a weak (N_2)(VO_2) complex.[6] This reaction provides an obvious method for catalytic removal of nitric oxide, and it will be of interest to compare the effectiveness of niobium and tantalum in this reaction.

The reactions of niobium and tantalum atoms with NO molecules are also of considerable interest, as niobium and tantalum nitrides have applications as semiconductors and coatings.[8] Synthesis of niobium and tantalum nitride thin films using different methods such as chemical vapor deposition, ion sputtering, and pulsed-laser deposition have been extensively studied.[9,10] Owing to the unusual thermostability of niobium and tantalum oxides, the possibility of oxygen contamination during film synthesis must be considered. One method for controlled oxygen addition to the Nb or Ta/N_2 system is to react with NO diluted in N_2. For this reason, a study of laser-ablated niobium and tantalum atom reactions with NO have been performed.

Experimental Section

The experiments of laser ablation and FTIR matrix investigation have been described previously.[11,12] The 1064 nm Nd:YAG laser beam (Spectra Physics, DCR-11) was focused by a 10 cm focal length lens onto the rotating metal target (Nb, Goodfellow, 99%; Ta, Mackay, 99.99%). The laser repetition rate is 10 Hz with a pulse width of 10 ns. Different laser powers ranging from 20 to 40 mJ/pulse at the sample were used in the experiments. The ablated metal atoms were co-deposited with 0.3%NO/Ar gas onto the 10 K CsI window at a rate of 2−4 mmol/h for 1−2 h. Different isotopic NO samples ($^{14}N^{16}O$, Matheson; $^{15}N^{16}O$, Isomet, 99%; $^{15}N^{18}O$, Isotec, 99%) and selected mixtures were used. FTIR spectra were recorded with 0.5 cm^{-1} resolution and 0.1 cm^{-1} accuracy on Nicolet 750.

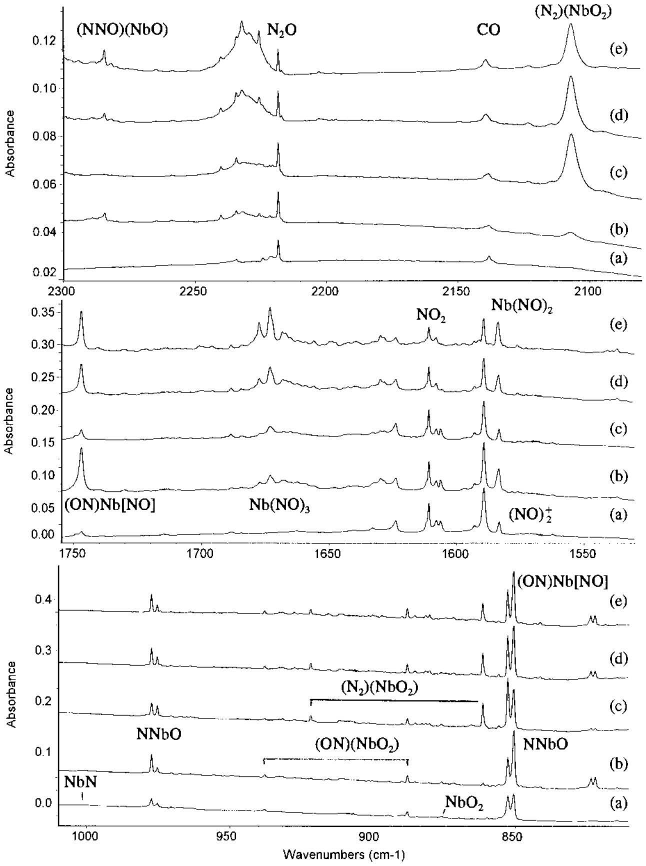

Figure 1. Infrared spectra for laser-ablated Nb atoms co-deposited with 0.3% NO in excess argon on a 10 K CsI window: (a) after 1 h sample co-deposition at 10 K; (b) after annealing to 25 K; (c) after broad-band photolysis for 30 min; (d) after annealing to 30 K; (e) after annealing to 35 K.

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TABLE 1: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Ablated Niobium Atoms with NO in Argon at 10 K

$^{14}N^{16}O$	$^{15}N^{16}O$	$^{15}N^{18}O$	$^{14}N^{16}O + ^{15}N^{16}O$	*R*(14/15)	*R*(16/18)	assignment
2284.2	2214.3	2205.6	2284.3, 2263.0, 2236.1, 2214.2	1.031 51	1.003 94	$(N_2O)(NbO)$
2232.2	2162.6			1.032 2		$X(N_2O)$
2218.4	2149.5	2142.5	2218.4, 2196.3, 2172.5, 2149.5	1.032 06	1.003 30	$(N_2O)(NbO)$
2107.0	2037.5	2037.5	2107.2, 2072.9, 2037.6	1.034 14		$(N_2)NbO_2$
1872.1	1839.1	1789.5	1872.1, 1839.0	1.017 94	1.027 72	NO
1863.3	1830.5	1781.2	1863.3, 1849.7, 1830.5	1.017 92	1.027 68	$(NO)_2$
1833.5	1802.1	1753.0		1.017 42	1.028 01	N_2O_3
1831.6	1799.4	1751.4		1.017 89	1.027 41	N_2O_3 site
1776.1	1744.6	1697.5	1776.1, 1757.6, 1744.7	1.018 06	1.027 75	$(NO)_2$
1747.1	1715.8	1697.5	1747.1, 1715.8	1.018 24	1.026 63	(ON)Nb[NO]
1677.5	1645.8	1604.9		1.019 26	1.025 48	$Nb(NO)_3$ site
1673.2	1642.5	1600.8	1673.4, 1662.5, 1651.2, 1642.6	1.018 69	1.026 05	$Nb(NO)_3$
1668.3	1637.6	1596.0		1.018 75	1.026 07	$Nb(NO)_3$ site
1610.8	1576.3	1545.7	1610.8, 1576.2	1.021 89	1.019 80	NO_2
1606.3	1571.8	1541.4	1606.3, 1571.8	1.021 95	1.019 72	NO_2 site
1589.3	1561.9	1520.4	1589.4, 1575.3, 1561.9	1.017 54	1.027 30	$(NO)_2^+$
1583.6	1555.3	1515.3	1583.9, 1567.8, 1555.4	1.018 39	1.026 20	$Nb(NO)_2$
1583.3	1556.0,	1514.6	1583.3, 1569.2, 1556.0	1.017 54	1.027 33	$(NO)_2^+$ site
1314.7	1295.5	1254.7		1.014 82	1.032 52	$(N_2O)(NbO)$
1301.4	1286.3					$(X)(N_2O)$
1296.2	1281.7	1234.6		1.011 31	1.038 15	N_2O_3
1282.7	1263.2	1224.0		1.015 44	1.032 03	N_2O
1243.5	1218.2	1191.8		1.020 77	1.022 15	NO_2^-
1222.7	1198.7	1172.1		1.020 02	1.022 69	cis-$(NO)_2^-$
1221.0	1199.9	1167.4		1.017 58	1.027 84	trans-$(NO)_2^-$
1135.4	1113.4	1089.0	1135.4, 1127.7, 1121.6, 1113.4	1.019 76	1.022 41	?
1002.9	973.7			1.029 99		NbN
1001.3	972.2			1.029 93		NbN site
1000.1	970.6			1.030 39		NbN site
977.3	951.9	947.0	977.3, 951.9	1.026 68	1.005 17	NNbO
975.3	950.3	944.9	975.3, 950.3	1.026 31	1.005 71	NNbO site
970.5	970.5	923.4			1.051 01	NbO
967.2	967.2	920.9			1.050 28	NbO site
965.0	965.0	918.6			1.050 51	NbO site
963.6	963.6	916.9			1.050 93	NbO site
937.8	937.8	891.0			1.052 53	$(ON)(NbO_2)$, ν_1
921.6	921.6	875.3		1.000 11	1.052 90	$(N_2)(NbO_2)$, ν_1
887.7	887.7	847.7			1.047 19	$(ON)(NbO_2)$, ν_3
875.8	875.9	835.6			1.048 23	NbO_2
869.8	869.7	830.0			1.047 83	NbO_2 site
861.4	861.3	822.3		1.000 12	1.047 43	$(N_2)(NbO_2)$, ν_3
852.6	849.7	813.8	852.6, 849.7	1.003 41	1.044 11	NNbO
850.6	848.0	811.7	850.6, 848.0	1.003 07	1.044 72	(NNbO)(NO)
843.2	839.7	805.3	843.2, 839.7	1.004 17	1.042 72	$(NNbO)(NO)_x$
841.3	838.0	803.2	841.3, 838.0	1.003 94	1.043 33	$(NNbO)(NO)_x$
823.4	808.0	793.8	823.4, 808.0	1.019 06	1.017 89	(ON)Nb[NO]
822.0	807.1	792.0	822.0, 807.2	1.018 46	1.019 07	site
768.3	784.3	745.4	768.3, 758.7, 748.3	1.026 73	1.003 89	N_2O_3

Matrix samples were annealed at different temperatures, and selected samples were subjected to broad-band photolysis by a medium-pressure mercury arc lamp (Phillips, 175 W) with the globe removed.

Results

Infrared spectra will be presented for Nb and Ta reactions with NO.

Nb + NO/Ar. Laser-ablated Nb atoms were co-deposited with 0.3% NO in argon, the spectra in the 2300−2080, 1755−1530, and 1010−810 cm^{-1} regions are shown in Figure 1, and the new product absorptions are listed in Table 1. In the lower cm^{-1} region, two pairs of doublets appeared at 977.3, 975.3 cm^{-1} and 850.6, 852.6 cm^{-1}; annealing to 25 K increased the stronger bands about 250% and the weaker bands about 70%. Broad-band photolysis decreased the stronger bands and increased the weaker bands. Another annealing to 30 K increased the stronger bands about 40% and slightly decreased the minor bands. The stronger bands held on the further annealing to 35 and 40 K, while the weaker bands decreased. A weaker pair of bands at 937.8 and 887.7 cm^{-1} were observed after deposition and increased 25% on first annealing, decreased 20% on photolysis, and increased together on further annealing. A sharp band at 861.4 cm^{-1} and a weak band at 921.7 cm^{-1} were produced on photolysis; these two bands decreased together on further annealing. A sharp doublet at 823.4 and 822.0 cm^{-1} was produced on annealing, destroyed on photolysis, and reproduced on annealing. In addition, weak absorptions at 1002.9 cm^{-1} due to NbN, 965.0 cm^{-1} due to NbO, and 875.8 cm^{-1} due to NbO_2 were observed after deposition.[13,14]

In the middle region, strong NO (1871.8 cm^{-1}) and $(NO)_2$ (1863.3, 1776.1 cm^{-1}) bands and NO_2 (1610.8, 1606.3 cm^{-1}) and $(NO)_2^+$ (1589.3, 1583.6 cm^{-1}) bands were observed after deposition.[15−17] Annealing to 25 K produced sharp bands at 1747.1, 1714.9 cm^{-1} together with a weak doublet at 1677.5, 1673.2 cm^{-1}. All these bands decreased on photolysis and increased on annealing. Meanwhile, a new 1583.6 cm^{-1} absorption near the $(NO)_2^+$ site band at 1583.3 cm^{-1} increased on 25 K annealing, which means that another new product band overlapped. In the ^{15}NO experiment, this band separated into

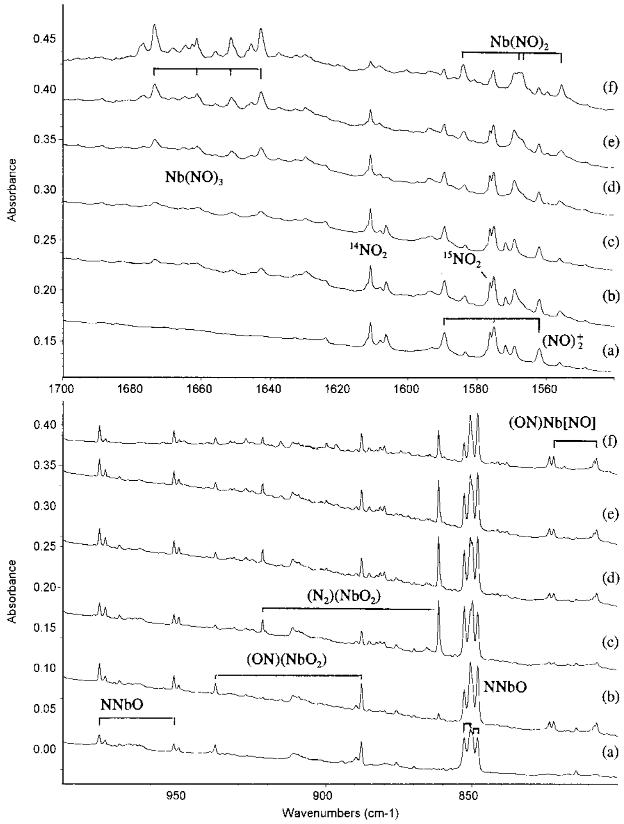

Figure 2. Infrared spectra for laser-ablated Nb atoms co-deposited with 0.15% ^{14}NO + 0.15% ^{15}NO in excess argon at 10 K: (a) after 1 h deposition; (b) after annealing to 25 K; (c) after 30 min broad-band photolysis; (d) after annealing to 30 K; (e) after annealing to 35 K; (f) after annealing to 40 K.

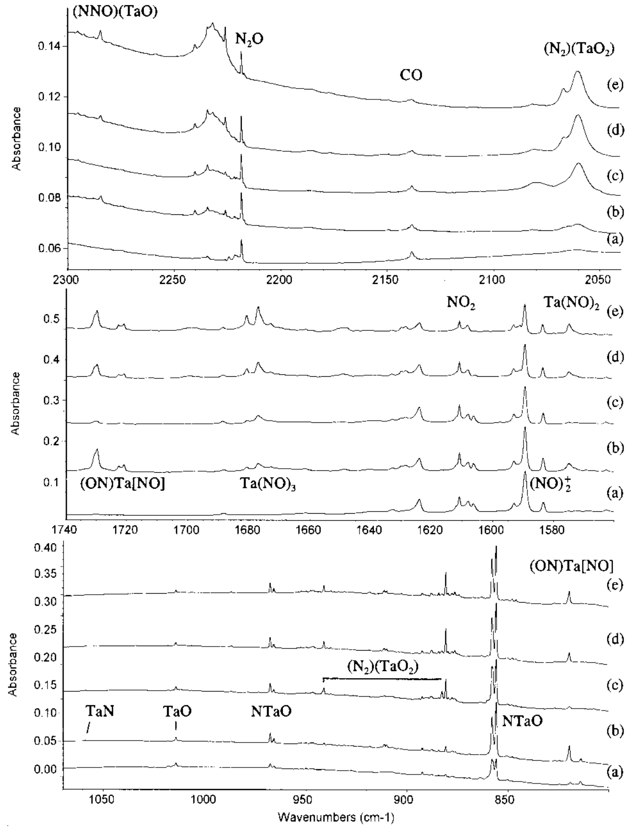

Figure 3. Infrared spectra for laser-ablated Ta atoms co-deposited with 0.3% NO in excess argon on a 10 K CsI window: (a) after 1 h sample co-deposition at 10 K; (b) after annealing to 25 K; (c) after broad-band photolysis for 30 min; (d) after annealing to 30 K; (e) after annealing to 35 K.

two discrete bands, which confirmed that the 1583.6 cm^{-1} band is a new product absorption. The band produced on annealing was destroyed on photolysis.

In the upper region, N$_2$O was observed on deposition and new bands appeared at 2284.2 and 2232.2 cm^{-1} on annealing. A new band at 2107.0 cm^{-1} increased markedly on photolysis and decreased slightly on annealing. This band tracked with the 861.4 and 921.7 cm^{-1} bands.

Experiments with ^{15}N^{16}O and ^{15}N^{18}O gave the same behavior with peaks shifted as listed in Table 1. One experiment with mixed ^{14}NO + ^{15}NO was done; doublets were observed for the 1747.1, 1714.9, 977.3, 975.3, 852.6, 850.6, 823.4, and 822.0 cm^{-1} bands, a triplet for the 2107.0 cm^{-1} band, and quartets for the 1673 and 1583.6 cm^{-1} bands. Figure 2 shows important regions in the mixed isotopic experiment.

Ta + NO/Ar. Laser-ablated Ta atoms co-deposited with NO in excess argon gave the infrared spectra shown in Figure 3; the absorptions are listed in Table 2. As can be seen, the spectra are very similar to those of the Nb + NO system. After deposition, two doublets at 967.6,965.9 and 857.9, 855.8 cm^{-1} were observed. The 967.6 and 855.8 cm^{-1} bands go together, both doubled on 25 K annealing, slightly decreased on photolysis, and increased about 15% on another annealing to 30 K. The 965.9 and 857.9 cm^{-1} bands behaved slightly differently; they doubled on annealing to 25 K, decreased more (25%) on photolysis, came back on annealing to 30 K, and held fast on further annealing to 35 and 40 K. A sharp band at 819.5 cm^{-1} produced on 25 K annealing, destroyed on photolysis, returned on higher temperature annealing, and tracked with the 1729.6 cm^{-1} band. A pair of bands at 941.0, 882.5 cm^{-1} which were very weak after deposition greatly increased on photolysis; stepwise annealing to 30, 35, and 40 K slightly increased and then decreased these bands; in the N−N stretching region, a new band at 2060.6 cm^{-1} exhibited matching behavior. Two weak bands at 819.1 and 814.1 cm^{-1} slightly decreased on annealing to 25 K and disappeared totally on photolysis. Meanwhile, very weak bands at 1058.8 cm^{-1} due to TaN and 1014.2 cm^{-1} due to TaO were observed after deposition[14,18] and decreased on annealing cycles, as in earlier matrix experiments. Important new bands at 1680.7, 1676.9, and 1574.8 cm^{-1} appeared on 25 K annealing in the upper region.

Again ^{15}NO and ^{15}N^{18}O experiments were done, and isotopic frequencies are listed in Table 2. An experiment with a ^{14}NO + ^{15}NO mixture revealed doublet isotopic structure for bands at 1729.6, 1058.8, 967.6, 965.9, 857.9, 857.5, 819.5, and 814.1 cm^{-1}, a triplet for 2060.6 cm^{-1}, and quartets for the 1676.9 and 1574.8 cm^{-1} bands. Selected regions of the mixed isotopic spectrum are shown in Figure 4.

Calculations. Density functional theory (DFT) calculations using the Gaussian 94 program[19] were employed to calculate structure and frequencies for the MNO isomers. The BP86 functional, D95* basis set for nitrogen and oxygen atoms and Los Alamos ECP plus double-ζ (DZ) basis set for metal atoms were used for all calculations.[20−22] These calculations are considered to be a first-order approximation and a guide for vibrational assignments. For both NbNO and TaNO isomers, the insertion products NNbO and NTaO molecules are calculated to be more stable than other isomers. The side bonded M[NO] and nitrosyl MNO isomers are about 40−50 kcal/mol higher in energy than corresponding NMO insertion products. Table 3 summarizes the calculated parameters.

TABLE 2: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Ablated Tantalum Atoms with NO in Argon at 10 K

$^{14}N^{16}O$	$^{15}N^{16}O$	$^{15}N^{18}O$	$^{14}N^{16}O + {}^{15}N^{16}O$	*R*(14/15)	*R*(16/18)	assignment
2284.3	2215.2	2205.5	2284.3, 2263.6, 2240.0, 2215.0	1.031 19	1.004 40	$(N_2O)(TaO)$
2079.5	2012.2					site
2060.6	1992.3	1992.0	2060.8, 2027.1, 1992.2	1.034 28		$(N_2)(TaO_2)$
1871.8	1838.8	1789.5	1871.8, 1838.8	1.017 95	1.027 55	NO
1863.3	1830.5	1781.2	1863.3, 1849.7, 1830.5	1.017 92	1.027 68	$(NO)_2$
1833.5	1801.2	1753.0		1.017 93	1.027 50	N_2O_3
1776.2	1744.8	1697.5	1776.2, 1757.6, 1744.7	1.018 00	1.027 86	$(NO)_2$
1729.6	1694.9	1655.8	1729.5, 1695.3	1.020 47	1.023 61	(ON)Ta[NO]
1720.8	1700.3	1647.8		1.012 06	1.031 86	(ON)Ta[NO]
1680.7	1649.3	1608.2		1.019 04	1.025 56	$Ta(NO)_3$ site
1676.9	1645.6	1604.7	1677.0, 1664.4, 1654.4, 1645.6	1.018 41	1.025 49	$Ta(NO)_3$
1610.8	1576.3	1545.7	1610.8, 1576.2	1.021 89	1.019 80	NO_2
1606.3	1571.8	1541.4	1606.3, 1571.8	1.021 95	1.019 72	NO_2 site
1589.3	1561.8	1520.4	1589.3, 1575.3, 1561.8	1.017 61	1.027 23	$(NO)_2^+$
1583.3	1556.0	1514.6	1583.3, 1569.2, 1556.0	1.017 54	1.027 33	$(NO)_2^+$ site
1574.8	1546.1	1507.0	1574.8, 1559.4, 1556.5, 1546.1	1.018 56	1.025 95	$Ta(NO)_2$
1296.2	1281.7	1234.6		1.011 31	1.038 15	N_2O_3
1282.7	1263.2	1224.0		1.015 44	1.032 03	N_2O
1243.5	1218.2	1191.8		1.020 77	1.022 15	NO_2^-
1222.7	1198.7	1172.1		1.020 02	1.022 69	cis-$(NO)_2^-$
1221.0	1199.9	1167.4		1.017 58	1.027 84	trans-$(NO)_2^-$
1058.8	1026.0	1026.0	1059.0, 1026.1	1.031 97		TaN
1018.2	1018.2	965.1			1.055 02	TaO site
1014.2	1014.2	961.4			1.054 92	TaO
1011.7	1011.7	959.0			1.054 95	TaO site
967.6	942.7	934.7	967.6, 942.7	1.026 41	1.008 56	NTaO
965.9	941.5	932.7	965.9, 941.6	1.025 92	1.009 43	NTaO site
941.0	941.0	890.8			1.056 35	$(N_2)(TaO_2)\ \nu_1$
918.4	918.2	870.4		1.000 22	1.054 92	(NO)TaO ?
911.1	904.3	869.1	911.1, 904.3	1.007 52	1.040 50	Ta[NO]
909.9	902.8	868.3	909.8, 902.8	1.007 86	1.039 73	Ta[NO]
907.6	907.6	861.3			1.053 76	$TaO_2\ (\nu_3)$
892.3	892.3	847.3			1.053 39	$(NO)_x(TaO_2)\ \nu_3$
887.9	887.9	842.9			1.053 50	$(NO)_xTaO_2\ \nu_3$
882.5	882.5	837.9			1.053 29	$(N_2)(TaO_2)$ site
880.6	880.6	836.2			1.053 10	$(N_2)(TaO_2)\ \nu_3$
857.9	852.7	816.2	857.9, 852.7	1.006 10	1.044 72	NTaO site
855.8	851.2	814.0	855.8, 851.2	1.005 63	1.045 49	NTaO
847.9	841.5	807.5	847.9, 841.5	1.007 61	1.042 11	(NO)NTaO
846.1	840.1	805.5	846.1, 840.1	1.007 14	1.042 95	(NO)NTaO site
819.5	800.7	788.7	819.5, 800.7	1.023 48	1.015 21	(ON)Ta[NO]
819.1	811.8	780.6		1.008 99	1.039 97	$(NTaO^-)$ site
814.1	807.8	775.5	814.1, 807.8	1.007 80	1.041 65	$(NTaO^-)$ site
787.5	765.4	760.8	787.5, 775.7, 765.4	1.028 87	1.006 05	?
783.7	764.9	759.4	785.7, 772.7	1.027 19	1.007 24	?
768.3	784.3	745.4	768.3, 758.7, 748.3	1.026 73	1.003 89	N_2O_3

Discussion

Similar products were observed for Nb and Ta, and these products will be assigned on the basis of isotopic shifts and splittings.

Insertion Products. *NNbO.* The doublets at 977.3, 975.3 and 852.6, 850.6 cm^{-1} are the major product absorptions; these bands go together throughout the experiments. Such small splittings are often observed in matrix samples and are ascribed to different argon packing arrangements or local “site” effects. The upper doublet shows large nitrogen (25.4 and 25.0 cm^{-1}) isotopic shifts and small oxygen (4.9 and 5.4 cm^{-1}) isotopic shifts. The observed nitrogen 14/15 isotopic ratios (1.0267, 1.0263) are slightly lower than the 1.030 value calculated for the diatomic NbN molecule, which characterizes a terminal Nb−N vibration with weak coupling to an O atom. In concert, the lower doublet has very small nitrogen (2.9 and 2.6 cm^{-1}) isotopic shifts and large oxygen (35.9 and 36.3 cm^{-1}) isotopic shifts. The oxygen 16/18 isotopic ratios (1.0441, 1.0447) are slightly lower than the calculated diatomic NbO ratio (1.051), which is suitable for a terminal Nb−O vibration with small coupling to an N atom. In the mixed 14−16/15−16 experiment, only pure isotopic counterparts are observed for all four bands. Accordingly, only one NO subunit is involved, and these bands are assigned to the NNbO molecule.

DFT calculations for singlet NNbO gave 1021.5 and 888.5 cm^{-1} for the N−NbO and NNb−O vibrational modes, which should be scaled by 0.96 to match the observed frequencies. The 14/15 and 16/18 isotopic frequency ratios observed for the upper and lower bands are in good agreement with the calculated (1.0282 and 1.0474) isotopic frequency ratios, which shows that the NNbO molecule characterized by the calculation has the same normal modes as the molecule assigned here.

Two very weak bands at 843.2 and 841.3 cm^{-1} have slightly higher nitrogen isotopic ratios and slightly lower oxygen isotopic ratios compared with the NNb−O vibration. The matrix site splitting (1.9 cm^{-1}) is almost the same as the site splitting of the 852.6 and 850.6 cm^{-1} bands. These two bands are assigned to the Nb−O vibration of a perturbed NNbO molecule, while the N−NbO mode is too weak to be observed. The source of this perturbation is probably NO in the (NNbO)(NO) complex.

NTaO. In the Ta + NO experiment, similar absorptions at 967.6, 965.9 cm^{-1} and 857.9, 855.8 cm^{-1} are assigned to the NTaO molecule. All these bands exhibit doublets in the mixed 14−16/15−16 experiment, indicating that only one N atom is

TABLE 3: Relative Energies (kcal/mol), Geometries, and Frequencies Calculated (BP86 Functional, D95* for N and O Atoms, Los Alamos ECP plus DZ on Metal Atoms) for NbNO and TaNO Isomers

molecule	rel energy	geom bond, Å	geom angle, deg	freq, cm^{-1} (intens, km/mol)
NNbO $^1A'$	0	NbN, 1.711; NbO, 1.765	∠NNbO, 104.0	384.9 (3), 888.5 (148), 1021.5 (41)
				378.6 (2), 886.9 (153), 993.5 (32)[a]
				369.9 (2), 846.8 (132), 990.4 (43)[b]
NbNO $^3\Delta$	+51.3	NbN, 1.800; NO, 1.226		356.7 (17), 621.6 (1), 1640.1 (526)
Nb[NO] $^3A'$	+55.3	NbN, 1.851; NbO, 1.915; NO, 1.449		540.0 (12), 659.3 (11), 950.2 (97)
				534.9 (11), 646.0 (11), 932.9 (941)[a]
				517.7 (12), 632.6 (9), 912.1 (90)[b]
NbNO $^5\Sigma^-$	+62.6	NbN, 1.872; NO, 1.219		284.8 (28), 550.1 (3), 1616.3 (396)
Nb[NO] $^1A'$	+65.6	NbN, 1.817; NbO, 1.855; NO, 1.500		504.0 (2), 724.7 (32), 948.1 (85)
Nb[NO] $^5A'$	+67.6	NbN, 1.983; NbO, 2.108; NO, 1.300		438.1 (11), 595.0 (3), 1229.9 (185)
NTaO $^1A'$	0	TaN, 1.728; TaO, 1.762	∠NTaO, 104.6	356.7 (2), 858.4 (86), 974.9 (0.1)
Ta[NO] $^1A'$	+38.0	TaN, 1.822; TaO, 1.830; NO, 1.532		446.6 (0.1), 759.1 (3), 934.8 (45)
TaNO $^1\Sigma^+$	+44.9	TaN, 1.773; NO, 1.222		397.3 (5), 633.0 (0.4), 1677.3 (568)
Ta[NO] $^3A'$	+47.8	TaN, 1.835; TaO, 1.890; NO, 1.487		539.2 (6), 663.0 (3), 921.9 (66)
TaNO $^3\Delta$	+51.7	TaN, 1.790; NO, 1.235		366.4 (14), 609.1 (0.4), 1617.2 (518)
TaNO $^5\Sigma^-$	+65.5	TaN, 1.851; NO, 1.227		284.6 (10), 549.1 (1), 1594.7 (346)
Ta[NO] $^5A'$	+69.1	TaN, 1.955; TaO, 2.077; NO, 1.325		424.2 (9), 612.1 (0.2), 1163.1 (131)

[a] Frequencies for $^{15}N^{16}O$ isotopic molecule. [b] Frequencies for $^{15}N^{18}O$ isotopic molecule.

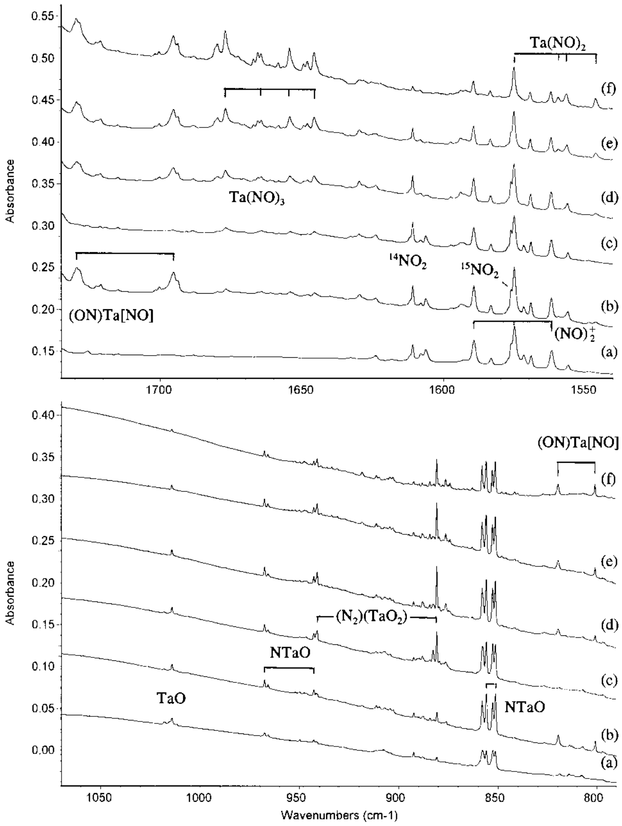

Figure 4. Infrared spectra for laser-ablated Ta atoms co-deposited with 0.15% ^{14}NO + 0.15% ^{15}NO in excess argon at 10 K: (a) after 1 h deposition; (b) after annealing to 25 K; (c) after 30 min broad-band photolysis; (d) after annealing to 30 K; (e) after annealing to 35 K; (f) after annealing to 40 K.

involved in these vibrations. The isotopic 14/15 ratios for the upper doublet (1.0264, 1.0259) are slightly lower than the diatomic TaN ratio (1.0325) and are suitable for a terminal Ta−N vibration with small coupling to an O atom, while, for the lower doublet, the large isotopic oxygen ratios (1.0447, 1.0455) and small nitrogen shifts are suitable for a terminal Ta−O vibration with small coupling to an N atom.

The weak bands at 847.9, 846.1 cm^{-1} have very similar isotopic ratios with the doublet at 857.9, 855.8 cm^{-1}; these two bands are attributed to the perturbed NTaO molecule.

DFT calculations support the assignment, because the frequencies calculated for singlet NTaO at 974.9 and 858.4 cm^{-1} are very close (0.99) to the experimental values. However, the calculated intensity of the Ta−N mode is unreasonably low. Of more importance, the observed 14/15 and 16/18 isotopic frequency ratios are in very good agreement with the ratios of calculated isotopic frequencies as a description of the normal modes.

Both NNbO and NTaO absorptions were observed as major products on deposition, so the insertion reaction is clearly favored. Both these absorptions increased on first annealing, so combination reactions of MO with N or MN with O atoms may occur in the matrix as both MO and MN absorptions were observed after deposition, and both decreased on annealing. However, the growth on annealing is probably large enough to suggest more insertion reaction.

NTaO$^-$. Two weak bands at 819.1 and 814.1 cm^{-1} were observed after deposition in the Ta + NO system. These bands were decreased slightly on 25 K annealing, totally destroyed on photolysis, and not reproduced on further annealing, which is characteristic behavior for charged species in the matrix. These bands show small nitrogen isotopic shifts; the 14/15 ratios 1.0078, 1.0090 are slightly higher than the NTa−O stretching vibration ratio of NTaO molecule, while the oxygen isotopic ratio 1.0417, 1.0400 is slightly lower than the NTaO ratio. No intermediate band was observed in the mixed isotopic experiment, which denotes the vibration of a single nitrogen atom. These bands are tentatively assigned to the NTaO molecular anions formed by electron capture.

Addition Products. The end- and side-bound addition products MNO and M[NO] are considerably higher in energy than the NMO insertion products, and no clear evidence is found here for the metal nitrosyl species. These molecules are weaker absorbers than the antisymmetric stretching modes of the higher nitrosyl species to be assigned below.

The weak 911.1, 909.9 cm^{-1} doublet in Ta experiments increases on first annealing, decreases substantially on photolysis, and increases on subsequent annealing cycles. The isotopic ratios are intermediate between Ta−O and Ta−N values, which is characteristic of the side-bound ring species. The strongest mode for Ta[NO] in the $^1A'$ ground state is 934.8 cm^{-1}.

Dinitrosyls. *Nb(NO)$_2$*. The absorption at 1583.6 cm^{-1} was produced on annealing. In the ^{15}NO experiment, this band shifts to 1555.0 cm^{-1} and the isotopic ratio 1.018 39 is very close to the diatomic NO ratio. In the mixed isotopic experiment, two close intermediate bands at 1567.8, 1566.9 cm^{-1} were observed, indicating that two slightly inequivalent N atoms are involved in the vibration, so the Nb(NO)$_2$ molecule with two nitrosyl ligands has a slightly asymmetric structure. In the V + NO system, V(NO)$_2$ has bent C_{2v} structure, and both symmetric and antisymmetric vibrations are observed.[6] The observed 1583.6 cm^{-1} frequency for Nb(NO)$_2$ was slightly lower compared to the 1614.0 cm^{-1} value for V(NO)$_2$ and 1623 cm^{-1} mode for Cr(NO)$_2$.[5,6]

Ta(NO)$_2$. The band at 1574.8 cm^{-1} in the Ta + NO system has the same behavior as the Nb(NO)$_2$ band in the Nb + NO system and is assigned to the Ta(NO)$_2$ molecule. This band was observed on annealing and decreased on photolysis. In the mixed experiment, two intermediate bands at 1559.4 and 1556.5 cm^{-1} were observed, which show only 2.9 cm^{-1} splitting, indicating that two inequivalent N atoms are involved. From the splitting, we can see that asymmetry in Ta(NO)$_2$ is larger than Nb(NO)$_2$.

Trinitrosyls. *Nb(NO)$_3$.* A new band appeared at 1673.2 cm^{-1} on 25 K annealing and increased significantly on higher temperature annealing. In the mixed isotopic experiment, a quartet with two weaker intermediate bands was produced, which is characteristic of a doubly degenerate mode.[23] The 1673.2 cm^{-1} band is assigned to the degenerate ν_3 mode of Nb(NO)$_3$ with the 1677.5 cm^{-1} splitting due to a different matrix site analogous to V(NO)$_3$ at 1715.1 cm^{-1}.[6]

Ta(NO)$_3$. In the Ta + NO system, the band at 1676.9 cm^{-1} with a 1680.7 cm^{-1} satellite also produced a quartet pattern with mixed ^{14}NO + ^{15}NO precursors, which identifies the degenerate vibration of three equivalent nitrogen atoms[23] and is assigned to the antisymmetric vibration of the Ta(NO)$_3$ molecule following the Nb(NO)$_3$ and V(NO)$_3$.

The trinitrosyls for V, Nb, and Ta are very similar. All have site structure with only 4−5 cm^{-1} splitting. The frequency of V(NO)$_3$ is slightly higher than the Nb and Ta nitrosyls, while Nb(NO)$_3$ and Ta(NO)$_3$ have only a 5 cm^{-1} difference.

Dioxide Complexes. *(N$_2$)(NbO$_2$).* The sharp bands at 921.7 tracks with the 861.4 cm^{-1} band and has 25% of the intensity; both bands increased on photolysis and showed no nitrogen isotopic shifts. The oxygen isotopic ratios, 1.0474 for the lower band and 1.0529 for the upper band, are almost the same as the calculated ratios for the antisymmetric and symmetric stretching vibrations of NbO$_2$, while the frequencies are 14.5 and 13.6 cm^{-1} lower than those for the NbO$_2$ molecule. So a perturbed NbO$_2$ molecule must be considered. Although isolated NbO$_2$ absorptions are very weak in the experiments, perturbation can effectively intensify the absorptions. Note the matching asymmetry in the Nb^{16,18}O$_2$ isotope for the two modes. In the 15−18 experiment, which was contaminated by 15−16, the intermediate band for the lower mode at 834.8 cm^{-1} is 7.1 cm^{-1} below the mean of pure isotopic values, and the intermediate of the upper mode at 905.6 cm^{-1} is 7.1 cm^{-1} higher than the mean of pure isotopic values. In the upper region, the band at 2107.0 cm^{-1} has the same annealing and photolysis behavior. This band showed a large nitrogen isotopic shift but no oxygen isotopic shift. The isotopic 14/15 ratio (1.0341) is very close to the dinitrogen ratio, and a symmetrical 1/2/1 triplet is observed in the mixed 14−15 experiment, indicating that two equivalent nitrogen atoms are involved. Accordingly, these three bands are suitable for the (N$_2$)(NbO$_2$) complex. Note that a similar species has also been observed in the V + NO system.

(NO)(NbO$_2$). The bands at 937.8 and 887.7 cm^{-1} observed after deposition increased slightly on annealing. These two bands show no nitrogen isotopic shift and symmetric and asymmetric NbO$_2$ isotopic ratios (1.0525, 1.0472). These two bands must be due to another kind of perturbed NbO$_2$ molecule, and NO molecule is the likely source of this perturbation.

The antisymmetric and symmetric stretching frequencies for NbO$_2$ are reported at 875.8 and 933.4 cm^{-1} in the argon matrix.[14] It is interesting to note that N$_2$ perturbed NbO$_2$ red shifts while NO perturbed NbO$_2$ blue shifts. In the Nb + O$_2$ system, (O$_2$)NbO$_2$ also blue shifts 28 and 12 cm^{-1} for antisymmetric and symmetric modes, respectively.[14]

(N$_2$)(TaO$_2$). Three bands at 2060.6, 880.6, and 941.0 cm^{-1} increased markedly on photolysis. Note the site structure for these bands: photolysis produced a site band at 882.5 cm^{-1} for the lower band, while for 941.0 cm^{-1} the site band cannot be resolved, but the band becomes broad, and the site band for 2060.6 cm^{-1} is at 2079.5 cm^{-1}. The 2060.6 cm^{-1} band did not shift with oxygen isotopic substitution but shifted with ^{15}NO and produced a triplet in the mixed 14−15 experiment with the 14/15 isotopic ratio of 1.0343, which is very close to the diatomic N−N ratio. On the contrary, the 880.6 and 941.0 cm^{-1} bands did not show a nitrogen isotopic shift, but a triplet was observed in the ^{15}N^{18}O experiment slightly contaminated by ^{15}N^{16}O. The triplets are also asymmetric: the intermediate for the lower mode is 8.4 cm^{-1} below the mean isotopic value, and the intermediate of the upper mode is 8.4 cm^{-1} above the mean value. The oxygen isotopic ratios (1.0533, 1.0564) are the same as the TaO$_2$ ratios.[14] These three bands are assigned to stretching vibrations of the (N$_2$)(TaO$_2$) molecule.

(NO)(TaO$_2$). The weak bands at 892.3, 949.9 cm^{-1} observed after deposition slightly decreased on annealing. These two bands show no nitrogen isotopic shifts and large oxygen shifts. The oxygen isotopic ratios (1.0534, 1.0550) indicate that these two bands are antisymmetric and symmetric vibrations of a TaO$_2$ molecule. Again, these two bands are assigned to a NO perturbed TaO$_2$ molecule following the (NO)(NbO$_2$) example. In contrast to the NbO$_2$ molecule, all of the perturbed TaO$_2$ molecules are red shifted. As can be seen, TaO$_2$ tends to form the (N$_2$)(TaO$_2$) complex in these experiments.

(ON)M[NO]. The 1747.1 and 823.4 cm^{-1} bands with Nb and 1729.6 and 819.5 cm^{-1} absorptions with Ta showed the same behavior. The bands increased markedly on 25 K annealing, decreased markedly on photolysis, and increased substantially on subsequent annealing. Furthermore these bands gave only doublets in mixed isotopic experiments, which indicates that each band is due to a single NO subunit.

The Nb band at 1747.1 cm^{-1} shifts to 1715.8 and 1697.5 cm^{-1} with ^{15}NO and ^{15}N^{18}O and exhibits the 14/15 ratio of 1.018 24 and the 16/18 ratio of 1.026 63. The Ta band at 1729.6 cm^{-1} exhibited the 14/15 ratio of 1.020 47 and 16/18 ratio of 1.023 61. These ratios characterize terminal N−O vibrations.

For the 823.4 cm^{-1} band, the 14/15 ratio of 1.0191 is higher than the N−O ratio, while the 16/18 ratio, 1.0179, is lower than the N−O ratio. These bands do not fit any structures of NbNO isomers, so a species containing two different NO subunits should be considered. The higher nitrogen isotopic ratio suggests that the 823.4 cm^{-1} band probably belongs to a bridged NO vibration. The band at 819.5 cm^{-1} in the Ta + NO reaction gave a large 14/15 isotopic ratio (1.0235) and small 16/18 ratio (1.015 21), also suggesting a metal vibration to the side-bound NO subunit.

The widely different frequency positions and isotopic frequency ratios show different bonding arrangements for each NO subunit, which are end- and side-bonded, respectively. These bands are assigned to (ON)Nb[NO] and (ON)Ta[NO], respectively.

Conclusions

Laser-ablated Nb and Ta atoms react with NO to give primarily the NNbO and NTaO insertion products, which are identified from isotopic substitution and density functional calculations of isotopic frequencies. Although the mononitrosyls are not observed, annealing gives dinitrosyls the trinitrosyls for both metals. Photolysis markedly increases $(N_2)(NbO_2)$ and $(N_2)(TaO_2)$ absorptions, which are due to stable end products for these reactions.

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References and Notes

(1) Blanchet, C.; Duarte, H. A.; Salahub, D. R. *J. Chem. Phys*. **1997**, *106*, 8778.

(2) Thomas, J. L. C.; Bauschlicher, C. W., Jr.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 8530.

(3) Fiedler, A.; Iwata, S. *J. Phys. Chem. A* **1998**, *102*, 3618.

(4) Ruschel, G. K.; Nemetz, T. M.; Ball, D. W. *J. Mol. Struct*. **1996**, *384*, 101.

(5) Zhou, M. F.; Andrews, L. *J. Phys. Chem. A* **1998**, *102*, 7452.

(6) Zhou, M. F.; Andrews, L. Submitted for publication (V + NO).

(7) Kushto, G. P.; Zhou, M. F.; Andrews, L.; Bauschlicher, C. W., Jr. Submitted for publication (Sc, Ti + NO).

(8) Tsai, M. H.; Sun, S. C.; Tsai, C. E. *J. Appl. Phys*. **1996**, *79*, 6932. Wang, Z.; Kawakami, A.; Uzawa, Y. *J. Appl. Phys*. **1996**, *79*, 7837.

(9) Cukauskas, E. J.; Qadri, S. B.; Carter, W. L. *J. Appl. Phys*. **1989**, *65*, 2053.

(10) Katz, A.; Pearton, S. J.; Nakahara, S. *J. Appl. Phys*. **1993**, *73*, 5208.

(11) Burkholder, T. R.; Andrews, L. *J. Chem. Phys*. **1991**, *95*, 8697.

(12) Andrews, L.; Burkholder, T. R.; Yustein, J. T. *J. Phys. Chem*. **1992**, *96*, 10182.

(13) Green, D. W.; Korfmacher, W.; Gruen, D. M. *J. Chem. Phys*. **1973**, *58*, 404.

(14) Zhou, M. F.; Andrews, L. *J. Phys. Chem. A*, in press. (Nb, Ta + O_2).

(15) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys*. **1971**, *55*, 3404.

(16) Hacaloglu, J.; Suzer, S.; Andrews, L. *J. Phys. Chem*. **1990**, *94*, 1759.

(17) Strobel, A.; Knoblanch, N.; Agreiter, J.; Smith, A. M.; Nerder-Schatteburg, G.; Bondybey, V. E. *J. Phys. Chem*. **1995**, *99*, 872.

(18) Bates, J. K.; Gruen, D. M. *J. Chem. Phys*. **1979**, *70*, 4428.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople J. A. *Gaussian 94*, *Revision B.1*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(20) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(21) Dunning, T. H., Jr.; Hay, P. J. in *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976.

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.

(23) Darling, J. H.; Ogden, J. S. *J. Chem. Soc., Dalton Trans*. **1972**, 2496.