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Reactions of Laser-Ablated Vanadium Atoms with Nitric Oxide. Infrared Spectra and Density Functional Calculations on NVO, V−η^1-NO, V−(η^1-NO)$_2$, V−(η^1-NO)$_3$, and V−η^2-NO

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Laser-ablated vanadium atoms have been reacted with NO molecules during condensation in excess argon. Absorptions due to NVO (998.1, 906.4 cm^{-1}), V−η^1-NO (1606.0 cm^{-1}), V−η^2-NO (1075.7 cm^{-1}) and V−(η^2-NO)$_2$ (1119.6,1153.8 cm^{-1}) are observed and identified via isotopic substitution and DFT calculations. Higher nitrosyls are also formed on annealing. On the basis of the observed isotopic splitting, bands at 1614.5 and 1736.8 cm^{-1} are assigned to antisymmetric and symmetric N−O vibrations of the C_{2v} dinitrosyl V(NO)$_2$, and 1715.1 and 1850.6 cm^{-1} bands are assigned to the analogous vibrations of V(NO)$_3$ with C_{3v} symmetry. The observation of (VO), (N$_2$O) and (N$_2$), (VO$_2$) complexes suggests that V atoms also react with (NO)$_2$ in these experiments.

1. Introduction

The chemistry of NO with transition metals is of great importance in synthesis, catalysis, surface science, and especially environmental science, as NO$_x$ compounds are significant pollutants from automobile exhausts.[1] The interaction of NO with metal surfaces has been the focus of intensive studies; these investigations have emphasized the characterization of molecular structure of NO on surfaces,[2] dynamics of dissociation, and reactions with other adsorbates.[3,4] Kinetics of transition metal atom reactions with NO and chemisorption and dissociation of NO on small transition metal clusters have also been performed in the gas phase.[5] In the matrix, reactions of NO with thermal atoms of late first row transition metals have been studied, and pure metal nitrosyls of Fe, Co, Ni, and Cu have been reported.[6] A recent matrix study of laser ablated chromium atom reactions with NO in this laboratory[7] observed both the insertion reaction to form NCrO and addition reactions to form cyclic Cr[NO] and the end-bonded nitrosyl CrNO. In addition, higher nitrosyls up to Cr(NO)$_4$ were also produced on annealing. In this paper we report a similar study on reactions of laser ablated vanadium atoms with NO molecules, which gives a similar distribution of products as chromium, and in addition evidence of more extensive reaction with (NO)$_2$.

2. Experimental Section

The experimental methods for of laser ablation and FTIR matrix investigation have been described previously.[8] The 1064 nm Nd:YAG laser beam(Spectra Physics, DCR-11) was focused by an 10 cm focal length focus lens onto the rotating vanadium metal target (Johnson Matthey, rod, 99.9%). The laser repetition rate is 10 Hz with pulse width of 10 ns. Different laser energies (20−40 mJ/pulse at the sample) were used in the experiments. The ablated metal atoms were codeposited with 0.025 to 0.4% NO in Ar gas onto the 10 K CsI window at a rate of 2−4 mmol/h for one to 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 a Nicolet 750 instrument using an MCTB detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis by a medium-pressure mercury arc lamp (Phillips, 175W) with globe removed (240−580 nm).

3. Results

Spectra of the laser-ablated vanadium atom reaction with NO products are shown in Figure 1 for selected wavenumber regions. The absorptions are listed in Table 1. After 1 h co-deposition of laser ablated V atoms with 0.4% NO in excess argon, strong absorptions of NO (1871.8 cm^{-1}), (NO)$_2$ (1863.3, 1776.2 cm^{-1}) together with N$_2$O (2218.4, 1282.8 cm^{-1}), (NO)$_2^+$ (1589.4 cm^{-1}), (NO)$_2^-$ (cis, 1222.7 cm^{-1}; trans, 1221.0 cm^{-1}) are observed.[9−12] Meanwhile, new absorptions at 1606.0, 999.8, 998.1, 937.8, 936.4, 906.4, and 896.3 cm^{-1} were also observed after deposition. On first annealing to 25 K, the absorptions at 999.8, 998.1, 937.8, 936.8, 906.4, and 896.3 cm^{-1} increased about 3-fold, while the 1606.0 cm^{-1} band increased 10-fold. New absorption bands at 1075.7, 1119.6, 1153.8, 1189.2, 1197.7, 1486.7, 1493.6, 1614.5, 1651.8, 1715.1, 1719.6, 1738.8, 2224.3, 2272.0, 2280.3, 2289.3, and 2298.0 cm^{-1} are produced during annealing to 25 K. Broad-band photolysis is done using medium pressure Hg arc lamp, as shown in Figure 1, photolysis slightly increased the 896.3, 906.4, 992.2 cm^{-1} bands and greatly increased the 937.8, 936.4, and 2280.3, 2272.0 cm^{-1} bands, while all other bands decreased. Upon further annealing to 30 K, all the decreased bands on photolysis are almost recovered, and the bands at 896.3, 906.4, 992.2, 937.8, 936.4, 2280.3, and 2272.0 cm^{-1} still keep slightly growing. Further annealing to 35 and 40K, only decreased the 906.4 and 997.8 cm^{-1} bands, while all other bands increased.

Experiments were done with ^{15}N^{16}O and ^{15}N^{18}O samples and the same behavior was observed. The isotopic frequencies are listed in Table 1. An experiment using a 50% ^{14}NO + 50%

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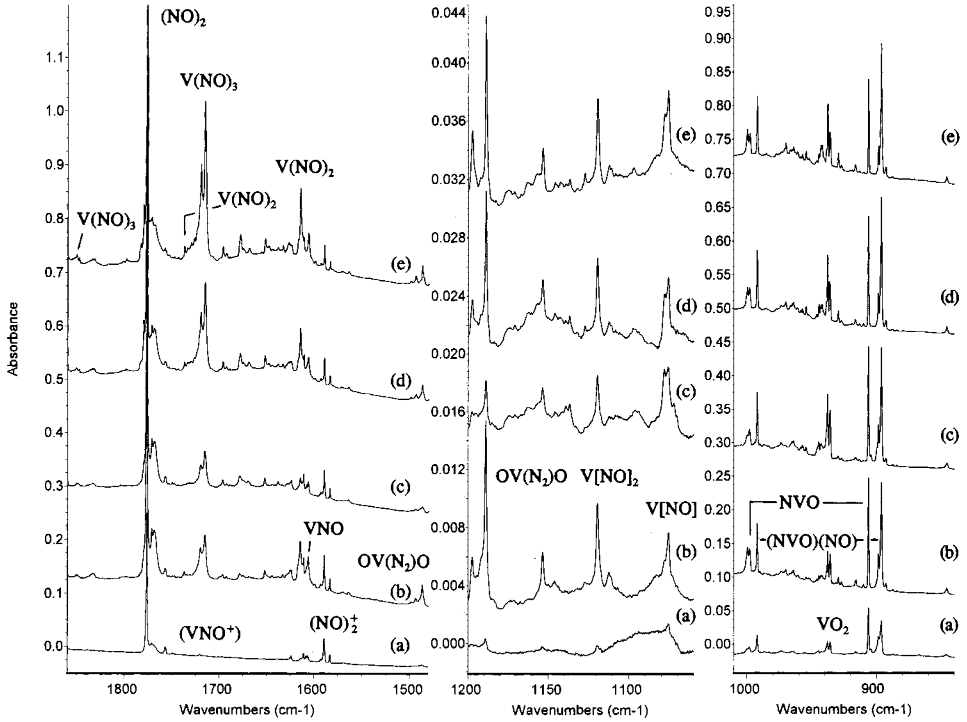

Figure 1. Infrared spectra for laser-ablated vanadium atoms co-deposited with 0.4% NO in excess argon on a 10 K CsI window. (a) after 1h sample co-deposition at 10 K, (b) after annealing to 25 K, (c) after broad-band photolysis for 30 min, (d) after annealing to 30 K, and (e) after annealing to 35 K.

^{15}NO mixture gave doublets for the 1606.0, 1075.7, 998.1, 992.2, 906.4, and 896.3 cm^{-1} bands, triplets for the 1119.6, 1614.5, 1651.8, 2272.0, and 2280.3 cm^{-1} bands, and quartets for the 2298.0, 2224.3, 1715.1, 1493.6, and 1189.2 cm^{-1} bands, also listed in Table 1. Selected spectral regions are shown in Figures 2 and 3.

4. Calculations

Density functional theory (DFT) calculations were performed on all the VNO isomers using Gaussian 94 program.[13] The BP86 functional[14,15] and 6-311+G* basis sets[16,17] for N, O and Wachter, Hay set[18] for V atoms were used. Calculated structures, relative energies and frequencies for low lying states of the V+NO isomers VNO, NVO, VON, and V[NO] are listed in Tables 2 and 3, respectively. Results for the VNO molecule are in very good agreement with the calculations recently reported.[19] A triplet ground state is predicted, while the quintet state is slightly higher in energy. Among the four isomers, singlet inserted NVO is the most stable; the triplet VNO and V[NO] and the quintet VON are 41.0, 45.4, and 74.9 kcal/mol higher than singlet NVO, respectively.

Similar calculations were also done for the higher V(NO)$_2$ and V(NO)$_3$ nitrosyls and the NVO(NO) complex. The calculations predict that the most stable $^2A_1$ state for V(NO)$_2$ has a bent geometry with the N−V−N angle of 90.1° and the most stable $^3A''$ state for V(NO)$_3$ is pyramidal with the N−V−N angle of 98.9°. The $^2A''$ NVO(NO) complex is 10.0 kcal/mol more stable than V(NO)$_2$, and the highest frequencies are 1704.4 cm^{-1} (623 km/mol), 962.7 (25), and 911.5 (246). The doublet (OV)(ONN) species converged to give the stable VO$_2$ and N$_2$ products.

5. Discussion

The new product absorptions will be identified and assigned based on isotopic substitution and DFT isotopic frequency calculations.

NVO. The absorptions at 998.1 and 906.4 cm^{-1} are the major absorptions produced on deposition. These two bands grew together on first annealing to 25 K and on photolysis, and decreased on further annealing to 35 and 40 K. The 998.1 cm^{-1} band shifts to 974.8 cm^{-1} in the ^{15}N^{16}O experiment and gives the 14/15 isotopic ratio of 1.0239, slightly lower than the diatomic V−N ratio (1.0272), while in the ^{15}N^{18}O experiment, this band shifts to 972.2 cm^{-1}, a small 2.6 cm^{-1} oxygen isotopic shift. In the mixed ^{14}NO + ^{15}NO experiment, a doublet is observed, indicating that this is a terminal V−N vibration with weak coupling to an oxygen atom. On the other hand, the 906.4 cm^{-1} band shows a large (35.2 cm^{-1}) oxygen isotopic shift and a very small (1.4 cm^{-1}) nitrogen shift. The isotopic 15/16:15/18 ratio 1.0404 is very close to the diatomic V−O ratio (1.045); again, only pure isotopic counterparts are observed in the mixed isotopic experiment. The isotopic ratios characterize the 998.1 and 906.4 cm^{-1} bands as almost pure V−N and V−O vibrational modes, respectively, and these absorptions are near those for isolated VN (1027.7 cm^{-1}) and VO (983.6 cm^{-1}) from recent V atom investigations in solid argon.[20,21] Analogous to the NCrO and NTiO insertion products,[7,22] the 998.1 and 906.4 cm^{-1} bands are assigned to the NVO molecule.

DFT calculations support the NVO assignment. First, the observed frequencies for the two modes are 0.92 and 0.95 times the calculated values. The calculated intensities of the two modes are 70/211, also in good agreement with the observed values (0.031/0.12). Finally, the calculated isotopic ratios (14/15 = 1.0258, 16/18 = 1.0023) for the upper mode and (14/15 = 1.0011, 16/18 = 1.0419) for the lower mode are in very good agreement with the observed ratios.

The bands at 992.2 and 896.3 cm^{-1} observed after deposition increased on subsequent annealing to 25, 30, 35, and 40 K at the expense of the NVO absorption. The upper band has the same isotopic ratios as the 998.1 cm^{-1} band, while the lower band has the same ratios as the 906.4 cm^{-1} band. Both bands exhibit doublets in the mixed isotopic experiment. Due to major

TABLE 1: Infrared Absorptions (cm^{-1}) from Codeposition of Laser-Ablated Vanadium Atoms with NO in Excess 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
2298.0	2227.2	2219.2	2298.1, 2276.2, 2250.1, 2227.3	1.031 79	1.003 63	$(N_2O)(VO)$
2289.3	2219.2	2212.6	2289.2, 2266.7, 2242.4 2219.2	1.031 58	1.003 01	$(N_2O)(VO)$
2280.3	2204.5	2204.3	2280.4, 2242.4, 2204.4	1.034 42		$(N_2)VO_2$
2272.0	2196.3	2196.4	2272.0, 2234.5, 2196.3	1.034 47		$(N_2)VO_2$
2224.3	2154.9	2148.1	2224.3, 2201.6, 2178.4, 2154.9	1.032 16	1.003 17	$X(N_2O)$
2218.4	2149.5	2142.5	2218.4, 2196.3, 2172.5, 2149.5	1.032 06	1.003 30	N_2O
1871.8	1839.0	1789.2	1871.8, 1839.0	1.017 84	1.027 83	NO
1863.3	1830.5	1781.2	1863.3, 1849.7, 1830.5	1.017 92	1.027 68	$(NO)_2$
1850.6	1815.4	1771.4	1841.4, 1827.5, 1815.4	1.019 40	1.024 79	$V(NO)_3$
1848.0	1812.8	1768.9	1812.7	1.019 38	1.024 83	$V(NO)_3$ site
1797.9	1765.8	1719.4		1.018 18	1.026 99	(NVO)(NO)
1776.2	1744.7	1697.5	1776.2, 1757.6, 1744.7	1.018 05	1.027 81	$(NO)_2$
1736.8	1703.3	1662.9	1736.8, 1721.9	1.019 67	1.024 29	$V(NO)_2$
1720.4	1686.0	1648.3		1.020 40	1.022 87	(VNO^+)
1719.6	1687.6	1645.4		1.018 19	1.025 67	$V(NO)_3$ site
1715.1	1683.2	1641.1	1715.1, 1702.3, 1692.0, 1683.1	1.018 19	1.025 66	$V(NO)_3$
1696.1	1664.1	1623.4		1.019 23	1.025 08	$V_x(NO)_y$
1677.8	1646.2	1605.2		1.019 16	1.025 57	$V_x(NO)_y$
1651.8	1620.1	1581.4	1651.8, 1633.4, 1620.1	1.019 55	1.024 46	$(V_2(NO)_2)$
1614.5	1585.4	1544.9	1614.5, 1598.0, 1585.4	1.018 34	1.026 25	$V(NO)_2$
1610.8	1576.3	1545.7		1.021 89	1.019 80	NO_2
1606.0	1574.2	1538.7	1605.9, 1574 sh	1.020 23	1.023 07	VNO
1589.4	1562.0	1520.4	1589.4, 1575.0, 1562.0	1.017 54	1.027 34	$(NO)_2^+$
1583.4	1556.3	1514.9	1583.4, 1569.5, 1556.3	1.017 46	1.027 32	$(NO)_2^+$
1493.6	1455.8	1438.2		1.025 99	1.012 22	site
1486.7	1449.0	1431.8	1486.8, 1479.8, 1455.4, 1449.0	1.026 07	1.011 98	$OV(N_2)O$
1321.3	1303.5	1261.2		1.013 66	1.033 54	site
1301.2	1282.0	1241.7	1301.2, 1298.6, 1284.6, 1282.1	1.014 98	1.032 46	$V_x(N_2O_3)$
1282.8	1263.1	1224.1		1.015 60	1.031 86	N_2O
1277.4	1258.1	1218.8		1.015 34	1.032 24	$X(N_2O)$
1243.5	1218.3	1192.0	1243.5, 1218.3	1.020 68	1.022 06	NO_2^-
1222.7	1198.7	1172.1	1222.7, 1209.4, 1198.7	1.020 02	1.022 69	*cis*-$(NO)_2^-$
1221.0	1199.9	1167.4	1221.0, 1209.4, 1199.9	1.017 58	1.027 84	*trans*-$(NO)_2^-$
1197.7	1167.4	1151.8		1.025 95	1.013 58	site
1189.2	1159.1	1143.5	1189.2, 1177.1, 1171.5, 1159.1	1.025 92	1.013 69	$OV(N_2)O$
1153.8	1133.3		1153.8, 1145.8, 1133.3	1.018 12		$V[NO]_2$
1119.6	1102.6	1075.3	1119.6, 1108.8, 1102.7	1.015 39	1.025 34	$V[NO]_2$
1075.7	1061.4	1030.8	1075.7, 1061.4	1.013 46	1.029 69	V[NO]
999.8	999.6	957.4		1.000 20	1.044 07	$(N_2O)(VO)$
997.7	997.5	955.7		1.000 20	1.043 74	$(N_2O)(VO)$
998.1	974.8	972.2	998.1, 974.8	1.023 90	1.002 75	NVO
992.2	968.2	965.8	992.2, 968.2	1.024 80	1.002 43	NVO(NO)
942.9	942.8	903.4		1.000 16	1.043 61	$(N_2)_xVO_2$
937.8	937.8	902.1			1.039 54	$(NO)VO_2$
936.4	936.4	900.9			1.039 42	$(NO)VO_2$
935.9	935.9	899.9			1.040 00	VO_2
906.4	905.0	869.8	906.4, 905.0	1.001 52	1.040 43	NVO
898.7	897.3	862.4		1.001 54	1.040 48	(NVO)(NO) site
896.3	895.1	860.0	896.3, 895.1	1.001 36	1.040 83	(NVO)(NO)
783.1	762.8	762.6	783.1, 773.6, 763	1.026 71	1.000 26	
764.3	746.7	741.7	764.3, 757.7, 753.5, 746.7	1.023 62	1.006 74	$OV(N_2)O$
741.7	736.6	713.3	741.7, 736.6	1.006 92	1.032 67	
625.2	614.3	607.1		1.017 16	1.011 86	
609.2	595.3	594.0		1.023 35	1.002 19	
575.8	570.1	562.4		1.010 00	1.017 83	
522.8	513.6	511.2		1.01722	1.004 69	

growth on high-temperature annealing, we prefer to identify these bands as NO complexed NVO instead of NVO at a different matrix site and to associate the 1797.9 cm^{-1} nitrosyl band with this species.

The NVO absorption is produced on deposition, so the insertion reaction 1 must be

$$V + NO \rightarrow (NVO)^* \xrightarrow{relax} NVO \qquad (1)$$

considered. Reaction 1 is highly exothermic (approximately 89 kcal/mol), as determined from DFT calculations, and this large excess reaction energy in the NVO molecules formed must be relaxed, or dissociation to VN or VO will follow. Since the VO and VN diatomic molecules were not observed here, relaxation by the argon matrix must be an efficient process. During codeposition, the argon serves as a third body to quench the large excess energy, and NVO is stabilized in the matrix. Since NVO absorptions increase markedly on first annealing (from 50% to 140% in different experiments) and slightly (10%) on photolysis, reaction 1 must be able to proceed with cold V atom insertion to form NVO, hence reaction 1 requires little activation energy. Although cold Cr atoms do not insert, cold Ti atoms react readily with NO on annealing to form NTiO.[7,22] The large yield of N_2O and NO_2 after deposition and the increase in these absorptions on first annealing indicate that both N and O atoms are produced and trapped in the matrix. The direct

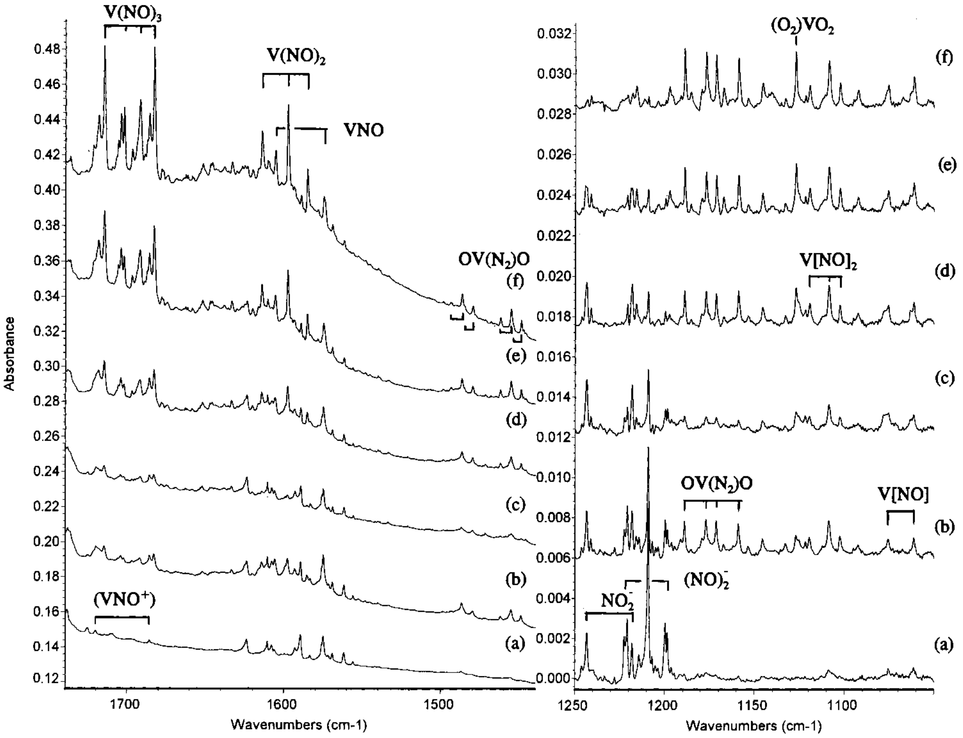

Figure 2. Infrared spectra in the 1740−1440 cm^{-1} and 1250−1050 cm^{-1} regions for laser-ablated vanadium atoms codeposited with 0.15% $^{14}N^{16}O$ + 0.15% $^{15}N^{16}O$ in excess argon at 10K. (a) after 1h deposition, (b) after annealing to 25 K, (c) after 30 min broadband photolysis, (d) after annealing to 30 K, (e) after annealing to 35 K, and (f) after annealing to 40 K.

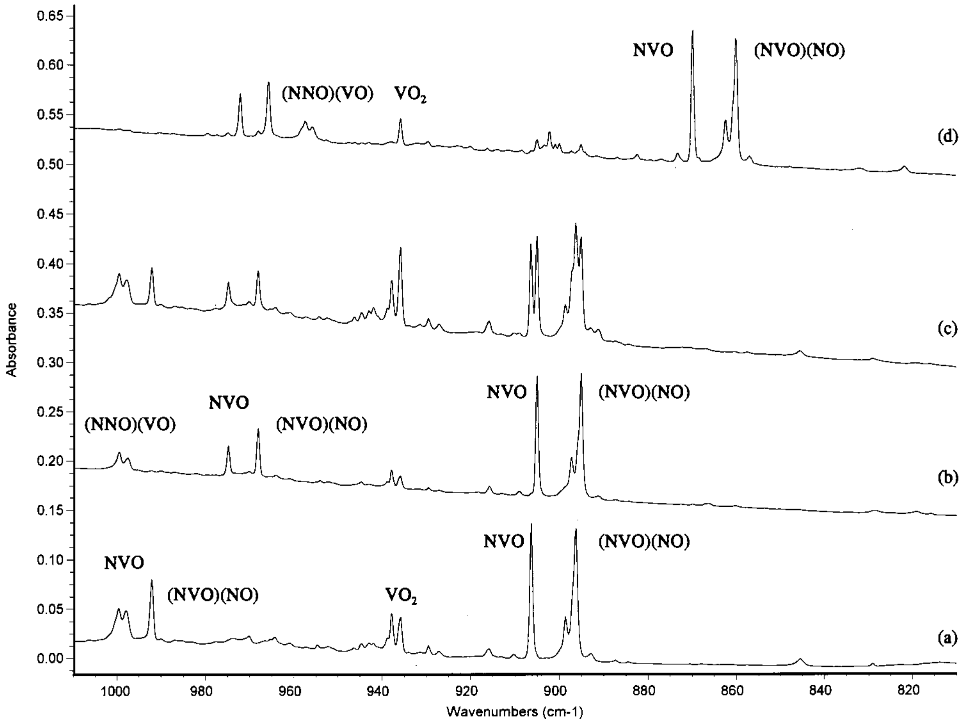

Figure 3. Infrared spectra in the 1010−810 cm^{-1} region for laser ablated vanadium atoms codeposited with 0.3 to 0.4% isotopic NO samples in excess argon after annealing to 25K. (a) $^{14}N^{16}O$, (b) $^{15}N^{16}O$, (c) mixed $^{14}N^{16}O$+$^{15}N^{16}O$, and (d) $^{15}N^{18}O$.

atom reaction 2 may contribute to the yield of NVO on annealing.

$$N + V + O \rightarrow NVO \qquad (2)$$

V−η^1-NO or VNO. The weak 1606.0 cm^{-1} band is the strongest new nitrosyl product band observed in the N−O stretching region after deposition. This band increased markedly on the first annealing cycle, while photolysis almost destroyed this band and NVO absorptions increased. In the $^{15}N^{16}O$ and $^{15}N^{18}O$ experiments, the 1606.0 cm^{-1} band shifts to 1574.2 and 1538.7 cm^{-1}. The 14/16:15/16 ratio 1.0202 is slightly higher than the diatomic NO ratio, while the 15/16:15/18 ratio 1.0231 is lower than the NO ratio, which show that the N atom is vibrating between O and another mass. In the mixed isotopic experiment, no obvious intermediate band is observed, and clearly, this band can be assigned to the VNO molecule. A

TABLE 2: Relative Energies and Bond Lengths Calculated (BP86/6-311+G*) for VNO Isomer and Ion States

molecule	state	relative energies (kcal/mol)	geometry(Å, deg)
NVO	$^1A'$	0.0	VN: 1.571 Å. VO: 1.632 Å. ∠NVO: 107.9°
VNO^-	$^2\Pi$	+10.8	VN: 1.667 Å. NO: 1.24.2 Å. ∠VNO: 180.0°
VNO^-	$^4\Sigma^-$	+18.4	VN: 1.716 Å. NO: 1.266 Å. ∠VNO: 180°
NVO	$^3A'$	+21.6	VN: 1.659 Å. VO: 1.616 Å. ∠NVO: 101.0°
VNO	$^3\Delta$	+41.0	VN: 1.677 Å. NO: 1.215 Å. ∠VNO: 180°
V[NO]	$^3A''$	+45.4	VN: 1.711 Å. VO: 1.831 Å. NO: 1.392 Å
VNO	$^5\Sigma^-$	+48.4	VN: 1.766 Å. NO: 1.204 Å. ∠VNO: 180°
V[NO]	$^5A'$	+49.7	VN: 1.868 Å. VO:1.953 Å. NO: 1.282Å
V[NO]	$^1A'$	+60.7	VN: 1.680 Å. VO: 1.740 Å. ON: 1.437Å
VON	$^5\Sigma^-$	+74.9	VO: 1.809 Å. ON: 1.228 Å. ∠VON: 180°
VON	$^3A''$	+79.3	VO: 1.791 Å. ON: 1.249 Å. ∠VON: 178.1°
VNO^+	$^2\Delta$	+211.9	VN: 1.697 Å. NO: 1.178 Å. ∠VNO: 180°
VNO^+	$^4\Sigma^-$	+214.5	VN: 1.782 Å. NO: 1.167 Å. ∠VNO: 180°

TABLE 3: Isotopic Frequencies (cm^{-1}), Intensities (km/mol), and Frequency Ratios Calculated (BP86/6-311+G*) for the Structures Described in Table 2

	14/16	15/16	15/18	*R*(14/16:15/16)	*R*(15/16:15/18)
NVO	421.4(3)	415.0(3)	405.8(3)	1.0154	1.0226
($^1A'$)	953.1(211)	952.1(218)	913.8(190)	1.0011	1.0419
	1083.5(70)	1056.2(57)	1053.8(75)	1.0258	1.0023
VNO	345.9(20)	337.2(18)	332.9(19)	1.0258	1.0130
($^3\Delta$)	646.1(1)	641.5(1)	625.6(1)	1.0071	1.0255
	1627.2(642)	1593.0(617)	1558.6(588)	1.0215	1.0221
V[NO]	464.5(6)	461.2(6)	446.3(6)	1.0072	1.0334
($^3A''$)	660.5(12)	646.1(11)	637.6(12)	1.0223	1.0133
	1006.9(146)	990.2(143)	966.3(132)	1.0169	1.0247
VNO^-	338.9(2)	330.4(2)	326.2(2)	1.0257	1.0129
($^2\Pi$)	654.8(0)	650.7(0)	633.5(0)	1.0063	1.0272
	1513.2(891)	1480.1(857)	1450.7(817)	1.0224	1.0203
VNO^+	321.3(4)	313.2(3)	309.2(4)	1.0259	1.0129
($^2\Delta$)	650.9(12)	645.7(2)	630.8(15)	1.0081	1.0236
	1787.9(352)	1751.9(336)	1711.2(323)	1.0205	1.0238

TABLE 4: Calculated (BP86/6-311+G*) Isotopic N−O Stretching Frequencies (cm^{-1}), Intensities (km/mol), and Frequency Ratios for the $V(NO)_2$ and $V(NO)_3$ Molecules

molecule	$^{14}N^{16}O$	$^{15}N^{16}O$	$^{15}N^{18}O$	*R*(14/15)	*R*(16/18)
$V(NO)_2$[a]	1649.7(1077)[c]	1616.4(1031)	1578.9(987)	1.0206	1.0238
($^2A_1$)	1731.3(527)[d]	1695.6(509)	1657.7(480)	1.0211	1.0229
$V(NO)_3$[b]	1668.3(1284)[c]	1635.8(1227)	1595.7(1178)	1.0199	1.0251
($^3A''$)	1766.9(188)[d]	1731.4(181)	1691.0(172)	1.0205	1.0239

[a] Structure: V-N, 1.722 Å; N-O, 1.196 Å; ∠NVN, 90.1°; ∠VNO, 179.7°. [b] Structure: V-N, 1.766 Å; N-O, 1.188 Å; ∠NVN, 98.9°, ∠VNO, 170.8°. [c] N−O antisymmetric stretching mode. [d] N−O symmetric stretching mode.

similar band at 1614 cm^{-1} was assigned to the CrNO molecule in the Cr+NO system.[7]

DFT calculations were done to support the assignment. The ground state for VNO is calculated to be triplet with linear structure, and the quintet is 7.4 kcal/mol higher than the triplet. The calculated NO stretching frequency for VNO, 1632.9 cm^{-1}, matches well with the observed 1606.0 cm^{-1} value. Of much more importance, however, is the very good agreement between the calculated (1.0215, 1.0221) and the above observed isotopic ratios, respectively, which characterize the normal mode and show that N is vibrating between metal and oxygen atoms. According to the calculation, there is a V−NO stretching mode at 646 cm^{-1}, but the intensity is too low to be observed in these experiments.

Due to the large energy separation between the NVO and VNO molecules, the relative yield of VNO is small after deposition as can be seen in the experiments. The VNO absorption increased dramatically on annealing, so reaction 3 can easily take place in the matrix without activation energy, whereas the insertion reaction to form NVO may require a small activation energy.

$$V + NO \rightarrow VNO \qquad \Delta E = -48\ \text{kcal/mol}^{19} \qquad (3)$$

$V-(\eta^1\text{-}NO)_2$ or $V(NO)_2$. The absorptions at 1736.8 and 1614.5 cm^{-1} track together; they are observed on first annealing to 25 K, almost destroyed on broadband photolysis, and come back on 30 K annealing, and keep growing together on further annealing. The intensity of the upper band is much weaker than the lower band. The upper band has a slightly higher nitrogen isotopic ratio (1.019 67) than the lower band (1.018 34), while the oxygen isotopic ratio is reversed, the upper band ratio 1.024 29 is slightly lower than the lower band 1.026 25 ratio. Both bands exhibit 1/2/1 triplets in the mixed isotopic experiment, which means that two equivalent NO submolecules are involved. The triplets are asymmetric: the intermediate component for the lower band is 2.0 cm^{-1} below than the mean of the $^{14}N^{16}O$ and $^{15}N^{16}O$ values, while the upper intermediate is 1.9 cm^{-1} above than the mean pure isotopic values, which is a consequence of interaction between the two stretching modes of $O^{14}N-V-^{15}NO$. These bands fit requirements for assignment to the symmetric and antisymmetric vibrational modes of the C_{2v} dinitrosyl $V(NO)_2$ molecule.

This assignment is supported by the DFT calculations. For $V(NO)_2$, no stationary point is found for the linear complex; the stable structure is C_{2v} with an NVN angle of 90.1°. The calculated symmetric and antisymmetric frequencies for the

$V(NO)_2$ molecule are 1731.3 and 1649.7 cm^{-1}, very close to the observed values, and the isotopic ratios are also in agreement.

V−(η¹-NO)₃ or V(NO)₃. The band at 1715.1 cm^{-1} observed on first annealing to 25 K, slightly decreased on photolysis, greatly increased on higher temperature annealing, and became the dominant band after 40 K annealing. This band was always accompanied by a site band at 1719.6 cm^{-1}. The 14/15 isotopic ratio 1.0189 is slightly lower than the mononitrosyl ratio, and the 16/18 ratio 1.0257 is slightly higher than the VNO ratio. In the mixed isotopic experiment, a quartet structure with two strong pure isotopic and two weaker intermediate bands is observed, indicating that three equivalent NO units are involved in a doubly degenerate vibration.[23] This band is assigned to the antisymmetric N−O stretching mode of the $V(NO)_3$ complex. It is difficult to determine structure without observing the symmetric stretching vibration, and the sharp 1850.6, 1848.0 cm^{-1} doublet is appropriate for the symmetric vibration, based on photolysis and annealing behavior, and on isotopic ratios. Clearly, the further addition reactions to form higher nitrosyls proceed readily, as found in the chromium system.[7]

$$VNO + NO \rightarrow V(NO)_2 \tag{4}$$

$$V(NO)_2 + NO \rightarrow V(NO)_3 \tag{5}$$

The trinitrosyl assignment is also supported by DFT calculations. Although the observed frequencies are 1.047 and 1.0281 times the calculated values, the 14/15 and 16/18 isotopic ratios are in excellent agreement with the calculated ratios. These isotopic ratios show how the N−O stretching normal modes change within the $V-(\eta^1\text{-NO})_x$ ($x = 1, 2, 3$) series to decrease nitrogen and increase oxygen participation with increasing number of nitrosyl ligands on the metal center.

V−η²-NO or V[NO]. The absorption at 1075.7 cm^{-1} appeared after 25 K annealing and retains essentially the same intensity on further annealing. The 14/15 ratio 1.0135 is lower than the diatomic NO ratio, while the 16/18 ratio 1.0282 slightly higher than the diatomic NO ratio, but still suggests an NO vibration. In the mixed isotopic experiment, no intermediate band is observed. So another VNO isomer must be considered. The VON molecule is calculated to be higher in energy than the other VNO isomers, and the frequency calculated for the most stable quintet state is higher than 1400 cm^{-1}. The calculation for the sideways bound $V-\eta^2$-NO or V[NO] molecule gives a triplet ground state, and the calculated frequency for NO stretching (1006.9 cm^{-1}) is close to the 1075.7 cm^{-1} experimental value. The calculated isotopic ratios 14/15 = 1.0169 and 16/18 = 1.0247 are slightly different from the observed values. This band is assigned to the $V-\eta^2$-NO molecule. which is in good agreement with recent results obtained for the Cr+NO system.[7] In that experiment, a 1108.8 cm^{-1} band is assigned to the similar $Cr-\eta^2$-NO molecule. Note that, for $Cr-\eta^2$-NO, the calculated frequency is also slightly lower than the experimental value, while the ratios are also slightly different from the observations. These cyclic molecules are not very easy to model theoretically, and higher level calculations are suggested.

The $V-\eta^2$-NO absorption increased on annealing, which means that this molecule can also be formed by the reaction of cold reagents in the matrix. Unlike $Cr-\eta^2$-NO, which was observed on deposition, the $V-\eta^2$-NO molecule can be observed only after annealing, this may be partly due to the great relative stability of the NVO molecule.

V−(η²-NO)₂ or V[NO]₂. The bands at 1119.6 and 1153.8 cm^{-1} produced on first annealing to 25 K, decreased about 50% percent on photolysis, and returned on further annealing. The 1119.6 cm^{-1} band is about four times stronger than the 1153.8 cm^{-1} band in the normal isotopic experiment. While in the $^{15}N^{18}O$ experiment, the counterpart of the 1153.8 cm^{-1} is too weak to be observed. The 14/15 isotopic ratio for 1119.6 cm^{-1} band is 1.0154, for the 1153.8 cm^{-1} band, the ratio is 1.0181, slightly higher than the 1119.6 cm^{-1} band. In the mixed experiment, both bands give 1/2/1 triplet structures. The intermediate counterpart for the lower band is 2.3 cm^{-1} lower than the mean pure isotopic values, while the intermediate for the upper band is 2.3 cm^{-1} higher than the mean pure isotopic values. Accordingly these two bands are suitable for symmetric and antisymmetric N−O vibrations of the $V-(\eta^2\text{-NO})_2$ molecule.

VNO⁺. The weak 1720.4 cm^{-1} band shifted with ^{15}NO and $^{15}N^{18}O$ giving isotopic ratios almost the same as VNO. Unfortunately, annealing markedly increased $V(NO)_3$, which covered the 1720.4 cm^{-1} band. However, with ^{15}NO the two absorptions are resolved, and photolysis decreases the 1686.0 cm^{-1} counterpart of the 1720.4 cm^{-1} band. Our DFT calculations predict the N−O fundamental of VNO^+ at 1787.9 cm^{-1} for the $^2\Delta$ ground state and isotopic frequency ratios in excellent agreement with the observed values.[24] The weak 1720.4 cm^{-1} band is tentatively assigned to VNO^+, which can be made by laser plume photoionization of VNO and the V^+ reaction with NO. The corresponding VNO^- anion was not detected, possibly due to photobleaching by the laser plume, although NO_2^- and $(NO)_2^-$ were observed in these experiments. Evidence for charged species was found in the Cr/NO system as well.[7]

(X)(N₂O). The bands at 2224.3 and 1277.4 cm^{-1} have the same isotopic ratios as the N_2O molecule, and the upper band is only 5.9 cm^{-1} higher than the N_2O frequency, while the lower band is 5.4 cm^{-1} below the N_2O frequency. These two bands are suitable for N_2O weakly perturbed by another molecule, and the observation of N_2O suggests that $(NO)_2$ may be the reagent.

(NNO)(VO). The doublet at 999.8 and 997.7 cm^{-1} increased on annealing. In the normal isotopic experiment, the 997.7 cm^{-1} band is overlapped with the NVO absorption at 998.1 cm^{-1}. Photolysis almost destroyed these bands while further annealing recovered them. The lower doublet showed 0.2 cm^{-1} nitrogen isotopic shifts, but large oxygen shifts; the isotopic 16/18 ratio 1.044 is very close to the diatomic VO ratio, which suggests a terminal V−O vibration with very weak coupling to nitrogen.

The bands at 2298.0 and 2289.3 cm^{-1} exhibit the same annealing behavior. Both have the same isotopic ratios as the N_2O molecule and a quartet structure in the mixed nitrogen isotopic experiment. These bands are due to strongly perturbed N_2O molecules, and the species NNO−VO is suggested.

$$V + (NO)_2 \rightarrow (NNO)(VO) \tag{6a}$$

(N₂)(VO₂). The doublet at 936.4 and 937.8 cm^{-1} increases on photolysis and annealing, and these bands show zero nitrogen isotopic shift. The oxygen isotopic ratio 1.0395 is almost the same as the ratio for VO_2, and the frequencies are only 0.5 and 0.9 cm^{-1} higher than the VO_2 frequency (935.9 cm^{-1}) observed in the argon matrix.[20] So these two bands must be due to weakly perturbed VO_2 molecules. Note that, in the N−N stretching region, two bands at 2280.3, 2272.0 cm^{-1} behave the same as these two bands. Both exhibit pure N−N stretching 14/15 ratios, and no oxygen shift. The mixed nitrogen isotopic experiment revealed triplets for both bands, indicating that two equivalent N atoms are involved. In the previous $V+N_2$ experiments, no bands were observed in this frequency region.[21] The frequencies are only about 50 cm^{-1} red shifted from to the diatomic N_2 frequency. Accordingly, we assign these two band pairs to the weak $(N_2)(VO_2)$ complex. This suggests that vanadium has reduced $(NO)_2$ to elemental nitrogen and invites consideration for the use of vanadium in the catalytic removal of NO from automobile exhausts.

$$V + (NO)_2 \rightarrow (N_2)(VO_2) \qquad (6b)$$

$OV(N_2)O$. The 1486.7, 1189.2, and 764.3 cm^{-1} bands increase together on annealing and decrease together on photolysis. These bands exhibit quartet absorptions in mixed $^{14}NO + ^{15}NO$ isotopic experiments showing two inequivalent N atoms in the vibrational modes. Assuming intact NO molecules, two inequivalent O atoms are also present. The large 14/15 ratios (1.02607, 1.02592, and 1.02362) indicate significant involvement of nitrogen. The most reasonable product for the above bands is the insertion of V into $(NO)_2$ to give a $OV(N_2)O$ species. Such an $OTi(N_2 \text{ ring})O$ species was found for titanium, and DFT calculations verified this structure, the frequencies, and isotopic ratios.[22] Attempts to calculate the $OV(N_2\text{-ring})O$ species gave the more stable NVO(NO) complex identified above.

The $(NO)_2$ dimer is present and grows markedly on annealing in these experiments and the chemical reaction of V with $(NO)_2$ is also expected in addition to the dinitrosyl $V(NO)_2$ complex. It is not surprising that perturbed N_2O is produced in these experiments, and loosely bound VO may be the perturbing molecule (possibly in a side−side orientation). However, much stronger interactions are required for the 2298.0, 999.8 cm^{-1} and 1486.7, 1189.2, 764.3 cm^{-1} band sets. The perturbed $(N_2)(VO_2)$, $(N_2O)(VO)$ and (NVO)(NO) species, of course, have the same stoichiometry. Vandium shares with titanium,[22] in contrast to chromium,[7] this more extensive reaction with $(NO)_2$, owing to the great stability of vanadium and titanium oxides.

Conclusions

Laser ablated vanadium atoms have been reacted with NO molecules during condensation in excess argon. Absorptions due to the insertion product NVO (998.1, 906.4 cm^{-1}) and the addition products $V-\eta^1\text{-NO}$ (1606.0 cm^{-1}), $V-\eta^2\text{-NO}$ (1075.7 cm^{-1}), and $V-(\eta^2\text{-NO})_2$ (1119.6, 1153.8 cm^{-1}) are observed and identified via isotopic substitution and DFT calculations. Higher nitrosyls are also formed on annealing: based on the observed isotopic splitting, bands at 1614.5 and 1736.8 cm^{-1} are assigned to antisymmetric and symmetric vibrations of C_{2v} $V(NO)_2$, and 1715.1 and 1850.6 cm^{-1} bands are assigned to antisymmetric and symmetric vibrations of C_{3v} $V(NO)_3$. The observation of several $(N_2)(VO_2)$, $(N_2O)(VO)$, $OV(N_2)O$, and NVO(NO) species suggests that vanadium reacts with $(NO)_2$ and points to the possible use of this metal in catalyst systems to remove NO from automobile exhaust gases.

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