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Reactions of laser-ablated chromium atoms with dioxygen. Infrared spectra of CrO, OCrO, CrOO, CrO3, Cr(OO)2, Cr2O2, Cr2O3 and Cr2O4 in solid argon

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Reactions of laser-ablated chromium atoms with dioxygen. Infrared spectra of CrO, OCrO, CrOO, CrO₃, Cr(OO)₂, Cr₂O₂, Cr₂O₃ and Cr₂O₄ in solid argon

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Reactions of laser-ablated Cr atoms with O_2 gave a very strong, sharp 965.4 cm⁻¹ band and weak, sharp 1869.7, 984.3, 914.4, 846.3, 716.2, and 643.1 cm⁻¹ bands. The 1869.7, 965.4, and 914.4 cm⁻¹ bands track together on annealing, show ⁵²Cr, ⁵³Cr, ⁵⁴Cr isotopic splittings appropriate for a single Cr atom and triplets with statistical ^{16,18}O₂ for two equivalent O atoms, and are assigned to the $\nu_1 + \nu_3$, ν_3 and ν_1 modes of the bent ($128^{\circ} \pm 4^{\circ}$) chromium dioxide OCrO molecule. The 984.3 cm⁻¹ band shows chromium isotopic splittings for two Cr atoms and ^{16,18}O₂ components for two O atoms, and is attributed to the bent CrOCrO molecule. The weak 846.3 cm⁻¹ band exhibits proper oxygen isotopic behavior for CrO and is redshifted 39 cm⁻¹ from the gas-phase value, the maximum shift observed for a first row transition metal monoxide. The sharp 716.2 and 643.1 cm⁻¹ bands track together; the former reveals Cr isotopic splittings for two Cr atoms and the latter ^{16,18}O₂ splittings for two sets of dioxygen subunits; the branched-puckered-ring dimer O(Cr₂O₂)O is identified. Annealing produces new bands due to CrOO, CrO₃, Cr(OO)₂ and the ring dimers (Cr₂O₂) and (Cr₂O₂)O, which are identified from isotopic shifts and splitting patterns. © *1997 American Institute of Physics*. [S0021-9606(97)01232-4]

INTRODUCTION

Chromium is one of the most important of the first row transition metals due to a wide range of applications in various fields of modern technology. The monoxide has been the most thoroughly studied gas phase molecule containing chromium.^{1–7} Several groups have investigated the matrix reaction of thermal chromium atoms and oxygen molecules^{8–10} as well as the photooxidation of $Cr(CO)_6$ in oxygen rich matrices.^{11–13} The former infrared work identified only the $Cr(OO)_2$ molecule, based on isotopic shifts and splitting patterns.⁸ Further investigations by Serebrennikov and Maltsev found the bent dioxide and many polymeric products.^{9,10} Earlier studies of the $Cr(CO)_6+O_2$ system identified the $(CO)_2CrO_2$ molecule,^{11,12} while later work suggested photoformation of OCrO in the matrix cage.¹³

Recent investigations of reactions of laser-ablated transition metal atoms with oxygen¹⁴⁻¹⁷ have shown very rich chemistry due to the high kinetic energy of the metal atoms.¹⁸ Accordingly, a different distribution of initial products is expected, compared to thermal evaporation experiments, and as a result, the appearance of new secondary reaction products. For example, the large yield of OCrO and CrO compared to thermal experiments leads to the dimers Cr₂O₂, Cr₂O₃, and Cr₂O₄, which were not observed previously. Furthermore, reactions of laser-ablated iron atoms with O₂ formed three FeO₂ isomers, which were identified with the help of electronic structure calculations,^{14,15} and the possibility of three isomeric structures must be considered for CrO₂ as well. With this in mind, it is very interesting to compare laser ablation and thermal evaporation experiments, which prompted the present reinvestigation of the Cr+O2 system.

EXPERIMENT

The techniques for laser ablation and FTIR matrix investigation have been described previously.^{15,19} Chromium (Johnson Matthey, lump, 99.2%) was mounted on a rotating (1 rpm) stainless steel rod. The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, 10 ns pulse width) was focused on the target through a hole in the CsI cryogenic (10 K) window. Laser power ranged from 40–50 mJ/pulse at the target. Metal atoms were codeposited with 0.25%–1.0% O₂ (and its isotopic modifications) in argon at 2–4 mmol/h for 1–3 h periods. FTIR spectra were recorded with 0.5 cm⁻¹ resolution and 0.1 cm⁻¹ accuracy on Nicolet 750. Matrix samples were temperature cycled, and more spectra were collected; selected samples were subjected to broadband photolysis by a medium pressure mercury arc (Phillips, 175 W with globe removed).

RESULTS

A. Infrared spectra

Spectra of the laser-ablated $Cr+O_2$ reaction system are presented in Fig. 1 for 1% O₂, and product bands are listed in Table I. After deposition, new 1869.7, 984.3, 973.7, 965.4, 914.4, 846.3, 844.8, 716.2, 643.1, and 599.1 cm⁻¹ bands were observed. The strong band at 965.4 cm⁻¹ was always accompanied by sharp, weak satellites at 962.4 and 959.5 cm⁻¹ and the weak 914.4 cm⁻¹ band exhibited satellites at 913.3 and 912.2 cm⁻¹. Photolysis increased the 1869.7, 965.4, and 914.4 cm⁻¹ bands by 20%; however, in a 0.25% O₂ experiment, these bands increased by a factor of 3 on photolysis. Annealing produced new 1153.9, 1134.2, 1108.7, 971.4, 968.4, 700.8, 684.8, and 628.2 cm⁻¹ bands,

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FIG. 1. Infrared spectra in the $1170-580 \text{ cm}^{-1}$ region for laser-ablated Cr atoms codeposited with 1% O₂ in argon. (a) 1 h reaction during deposition at 10 K, (b) after annealing to 25 K, (c) after annealing to 35 K, and (d) after annealing to 40 K. Arrows indicate chromium isotopic satellites.

increased the 984.3, 716.2, and 648.1 cm⁻¹ bands, and decreased the 1869.7, 973.7, 965.4, 914.4, 846.3, and 844.8 cm⁻¹ bands.

Oxygen isotopic substitution was employed for band identification. Isotopic spectra including mechanical $({}^{16}O_2 + {}^{18}O_2)$ and statistical $({}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2)$ mixtures are presented in Figs. 2-5. The 1153.9 and 1134.2 cm⁻¹ bands grew markedly on annealing and produced together 11 components, which will be discussed in the next section. The 1108.7 cm⁻¹ band produced on first and decreased on second annealing was weak, but intermediate components were found (Fig. 2). The 984.3, 965.4, 914.4, and 628.2 cm⁻¹ bands produced triplets with scrambled oxygen. The 1869.7, 965.4, and 914.4 cm^{-1} bands produced doublets and 1:2:1 triplets with mechanical and statistical mixtures, respectively (Fig. 3). The 968.4 cm^{-1} band produced a quartet isotopic structure on annealing (Fig. 4). The 716.2 cm^{-1} band gave a sharp triplet with the mechanical mixture but a broadened shifted triplet with scrambled oxygen. The 700.8 cm⁻¹ band produced a triplet of doublets with the mechanical and statistical mixtures. The 643.1 cm⁻¹ band produced a nonet with scrambled oxygen and a triplet with the mechanical mixture (Fig. 5). Other bands and their isotopic patterns are listed in Table I.

Supplemental experiments were also done with N_2O/Ar and O_2/N_2 mixtures. The first system gave moderate 973.7,



FIG. 2. Infrared spectra in the $1160-1042 \text{ cm}^{-1}$ region for laser ablated Cr atoms codeposited with mixed isotopic oxygen samples at 10 K. (a) ${}^{16}\text{O}_2+{}^{18}\text{O}_2$ (0.5%+0.5%) after annealing to 25 K, (b) after annealing to 35 K, (c) ${}^{16}\text{O}_2+{}^{16}\text{O}^{18}\text{O}+{}^{18}\text{O}_2$ (0.125%+0.25%+0.125%) after annealing to 25 K, and (d) after annealing to 30 K.

970.2, and 965.4 cm⁻¹ bands and weak 968.4, 914.4, 879.6, 856.9, 846.3, and 643.1 cm⁻¹ bands upon deposition. Annealing increased the 973.8, 968.8, and 879.8 cm⁻¹ bands and decreased all other bands. The yield of CrO (846.3 cm⁻¹) was enhanced relative to the yield of OCrO (965.4 cm⁻¹). In the O_2/N_2 system, analogous sharp bands at 976.3 and 973.3 cm⁻¹ and a weak 866.6 cm⁻¹ band were observed.

B. Calculations

High level calculations (CCSD(T)) performed on CrO revealed a ${}^{5}\Pi$ state with a 1.633 Å bond length and 888 cm⁻¹ harmonic frequency in excellent agreement with experiment.⁷ We employed the GAUSSIAN 94 program²⁰ to do DFT calculations of geometry and vibrational frequencies for CrO₂ isomers using the B3LYP approximation at low cost as a guide for making vibrational assignments. The 6-311G* basis sets were used for both oxygen and chromium atoms. First as a calibration, this approximate calculation yielded a 1.615 Å bond length and 868 cm⁻¹ harmonic frequency for the lowest quintet state of CrO. Clearly, these DFT/B3LYP calculations are a reasonable approximation. Using a larger



FIG. 3. Infrared spectra in the 1880–1780 and 980–910 cm⁻¹ regions for Cr codeposited with isotopic oxygen samples in excess argon after annealing to 25 K to optimize CrO_2 absorptions. (a) ${}^{16}O_2$. 0.5%, (b) ${}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$, 0.5%, (c) ${}^{16}O_2 + {}^{18}O_2$, 0.5% + 0.5%, and (d) ${}^{18}O_2$, 0.5%. Weak H₂O vibration–rotation lines are noted (*) in the spectra.

basis set $(6-311+G^*)$ for CrO gave a 1.648 Å bond length and 898 cm⁻¹ harmonic frequency, in exact, although fortuitous, agreement with experiment.¹

Results are presented in Table II for CrO_2 isomers using the 6-311G* basis sets. For the bent OCrO molecule, the ground state is triplet. For cyclic $Cr(O_2)$, singlet, triplet, quintet, and septet states were calculated, and found to be higher than OCrO by 132, 74, 56, and 81 kcal/mol, respectively. For bent CrOO, quintet and septet states are higher than OCrO by 67 and 83 kcal/mol, respectively. Although agreement between calculated and observed spectra for OCrO is excellent, these calculations are considered only as a first approximation, and higher levels of theory and more sophisticated basis sets need to be employed.

DISCUSSION

Identification and assignment of chromium oxide molecular species follow.

CrO

The weak 846.3 cm⁻¹ band was observed in the spectra after deposition and decreased upon annealing; its intensity was enhanced relative to the 965.4 cm⁻¹ band (OCrO) in experiments with N₂O. The 846.3 cm⁻¹ band produced doublets with both mechanical and statistical mixtures, and the (16/18) isotopic ratio 1.0453 is very close to the theoretical



FIG. 4. Infrared spectra in the $1020-910 \text{ cm}^{-1}$ region for Cr codeposited with statistically mixed (${}^{16}\text{O}_2 + {}^{16}\text{O}{}^{18}\text{O}_2$) oxygen (0.5%) in argon. (a) after deposition at 10 K for 1.5 h, arrows indicate chromium isotopic satellites, and (b) after annealing to 40 K, slashes divide band absorbance—above slash is growth at this frequency on annealing.

harmonic diatomic ratio (1.0455). Based on these results, the 846.3 cm⁻¹ band is assigned to the CrO molecule. Gas phase experiments found a 885 cm⁻¹ fundamental.¹⁻³ The large matrix shift can be probably explained by high polarizability



FIG. 5. Infrared spectra in the 720-600 cm⁻¹ region for the same isotopic mixtures used in Fig. 3 after annealing to 35 K to optimize product bands in this region.

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TABLE I. Infrared absorptions (cm⁻¹) observed for the laser-ablated $Cr+O_2$ system in solid argon.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$rO(\nu_{1} + \nu_{3})$ $rO(\nu_{1} + \nu_{3})$ $rO(\nu_{1} + \nu_{3})$ $rO(\nu_{1} + \nu_{3})$ rOO rOO rOO rOO rOO site rOO isomer
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$rO(\nu_{1} + \nu_{3})$ $K-(O_{2})_{n}$ $CrOO$ rOO $CrOO site$ $rOO isomer$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$(O_2)_n$ CrOO OCrOO CrOO site rOO isomer
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CrOO OCrOO CrOO site rOO isomer
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	OCrOO CrOO site rOO isomer
1109.8, 1103.2, 1096.1, <i>1078.5</i> , 1070.8 1126.7 1064.2 1.0587 + OO	CrOO site rOO isomer
1126.7 1064.2 1.0587 + 0.00	CrOO site rOO isomer
	rOO isomer
1108.7 1046.7 <i>1125, 1108, 1056, 1047</i> 1.0592 +,- OOC	
1044.8 1001.8 1044, 1036, 1013, 1002 1.0429 +	Cr_2O_3
1039.5 982.4 <i>1039.5</i> , 1025.5, 1016.0, 1.0581 - 1006.2, 991.7, 982.4 -	O ₃
1027.2 985.7 1.0421 +	Cr_xO_y
984.3 943.2 1007.7, 984.3, 954.8, $1.0436 + {}^{52}C$ 943.2	CrO ⁵² CrO
983.0 941.9 983.0, 941.9 $1.0436 + {}^{52}C$	CrO ⁵³ CrO
981.8 940.7 981.8, 940.7 1.0437 + 52 C	CrO ⁵⁴ CrO
973.7 936.8 973.7, 962.5, 936.8 1.0394 - 0	OOCrO ₂
971.4/970.2 934.5/933.7 971.4, 934.6 1.0395 + 0	OOCrO ₂
968.4 932.1 968.4, 960.2, 950.7, 1.0389 + 932.1 +	CrO ₃
967.6 930.8 966.5, 930.2 1.0394 + CrC	D_2 site(ν_3)
965.4 929.2 965.4, 953.6, 929.2 $1.0394 + - 520$	$\operatorname{CrO}_{2}(\nu_{3})$
962.4 926.1 962.4, 950.6, 926.1 $1.0392 + - 530$	$\operatorname{CrO}_{2}(\nu_{3})$
959.5 923.1 959.5, 947.7 $1.0394 + - {}^{54}$	$\operatorname{CrO}_{2}(\nu_{3})$
956.8 917.5 1.0463 +	Cr,O,
934.3 898.0 1.0404 -	Cr_rO_v
914.4 869.7 914.4, 885.6, 869.7 $1.0514 + {}^{52}$	$\operatorname{CrO}_2(\nu_1)$
913.3 868.5 913.3, 884.2, 868.5 $1.0516 + {}^{53}$	$\operatorname{CrO}_{2}(\nu_{1})$
912.2 867.3 882.8 $1.0518 + {}^{54}$	$\operatorname{CrO}_{2}(\nu_{1})$
846.3 809.6 846.3, 809.6 1.0453 -	⁵² CrO
844.8 800.1 844.8, 833.2, 806.6, 1.0559 - (C 800.1	CrCrOO)
831.3w 795.9 831.3 1.0445 + (($Cr_2O_2O_2$
804w 765 804, 765 1.0510 - (r	CrOCr)
761br 730br 761, 730 1.0425 - ($(Cr_{y}O_{y})$
716.2 686.8 715.9, 711.4, 687.0 $1.0428 + O(52)$	$Cr^{52}CrO_2)O$
715.3 685.9 715.3, 685.8 $1.0429 + O(^{52}C)$	$Cr^{53}CrO_{2}O$
714.4 685.0 714.4, 685.0 $1.0429 + O(^{52}C)$	$Cr^{54}CrO_{2}O$
700.8 673.9 700.8, 698.9, 683.9, 1.0399 + (0	$Cr_2O_2O_2$
683.0, 675.3, 673.9	2 2
684.8w 656.6 684.8, 669.9, 668.8, 1.0430 + 656.6	?
643.1 611.4 <i>643.1</i> , 641.3, 639.7, 1.0519 + O($(Cr_2O_2)O$
629.4, 627.7, 626.1, 614.8, 613.1, <i>611.4</i>	2-2/-
628.2 601.3 619.7, 601.3 1.0447 + ((Cr_2O_2)
599.1 576.0 1.0401 +	Cr_xO_y

^aItalic bands observed prominently with ${}^{16}O_2 + {}^{18}O_2$ mixture.

of the ⁵ Π ground state^{3,7} of CrO. The formation of CrO on deposition and subsequent decrease on annealing indicates that reaction (1) requires significant activation energy, which is expected for this endothermic (by 17 kcal/mol)¹ reaction. Thus CrO is formed by the reaction of highly energetic laserablated chromium atoms¹⁸ but is not formed to any appreciable extent by Cr atoms in the matrix

$$Cr+O_2 \rightarrow CrO+O \quad \Delta E = +17 \text{ kcal/mol.}$$
 (1)

Note also that no CrO was detected in previous experiments with thermally evaporated chromium atoms.⁸⁻¹⁰ As de-

scribed above, the yield of CrO was enhanced in the $Cr+N_2O$ system compared to the $Cr+O_2$ system. Reaction (2) is exothermic (by 61 kcal/mol)

$$Cr+N_2O \rightarrow CrO+N_2 \quad \Delta E = -61 \text{ kcal/mol.}$$
 (2)

After codeposition with the N_2O/Ar mixture, a new strong 856.9 cm⁻¹ band was observed together with the 846.3 cm⁻¹ band. The former band is assigned to the NNCrO complex by analogy with similar results in the Fe and Co systems^{15,17}. Note also that a 866.3 cm⁻¹ band was assigned to the OCCrO molecule in the Cr+CO₂ system based on

Molecule	Geometry (Å, deg)	$\nu_1(I)$	$\nu_2(I)$	$\nu_3(I)$
¹⁶ OCr ¹⁶ O ³ B ₁ , 0 kcal/mol	$R(Cr-O) = 1.586, \alpha = 125^{\circ}$	1025(28)	276(22)	1071(366)
¹⁶ OCr ¹⁸ O		992(66)	270(21)	1059(315)
¹⁸ OCr ¹⁸ O		975(26)	264(20)	1030(340)
$Cr({}^{16}O_2)$, ${}^{1}A_1$, +132 kcal/mol	R(Cr-O) = 1.779,	897(199)	666(68)	494(9)
$Cr(^{16}O^{18}O)$	$R(O-O) = 1.454, \alpha = 48^{\circ}$	874(194)	653(62)	480(9)
Cr(¹⁸ O ₂)		850(188)	639(58)	468(8)
$Cr({}^{16}O_2), {}^{3}B_1, +74 \text{ kcal/mol}^a$	R(Cr-O) = 1.903	1189(102)	428(0)	312(3)
Cr(¹⁶ O ¹⁸ O)	$R(O-O) = 1.315, \alpha = 40^{\circ}$	1156(96)	421(0)	303(3)
$Cr(^{18}O_2)$		1121(91)	4132(0)	295(3)
$Cr({}^{16}O_2), {}^{5}B_2, +56 \text{ kcal/mol}$	R(Cr-O) = 1.820	919(67)	608(25)	575(15)
Cr(¹⁶ O ¹⁸ O)	$R(O-O) = 1.456, \alpha = 47^{\circ}$	895(65)	599(22)	558(16)
$Cr(^{18}O_2)$		869(62)	586(22)	545(15)
$Cr({}^{16}O_2), {}^{7}A_2, +81 \text{ kcal/mol}$	R(Cr-O) = 2.088	1161(6)	463(76)	979(113)
$Cr(^{16}O^{18}O)$	$R(O-O) = 1.351, \alpha = 38^{\circ}$	1129(6)	755(73)	952(107)
Cr(¹⁸ O ₂)		1095(5)	447(7)	926(102)
Cr ¹⁶ O ¹⁶ O, ⁵ A", +67 kcal/mol	R(Cr-O) = 1.853,	1165(143)	128(10)	526(7)
Cr ¹⁶ O ¹⁸ O	$R(O-O) = 1.318, \alpha = 104$	1132(133)	123(10)	525(7)
Cr ¹⁸ O ¹⁶ O		1133(137)	127(10)	503(7)
Cr ¹⁸ O ¹⁸ O		1099(127)	122(10)	503(7)
$Cr^{16}O^{16}O$, ⁷ <i>A</i> ', +83 kcal/mol	R(Cr-O) = 1.888,	1141(15)	201(7)	540(68)
Cr ¹⁶ O ¹⁸ O	$R(O-O) = 1.337, \alpha = 117$	1110(15)	194(7)	537(68)
Cr ¹⁸ O ¹⁶ O		1108(13)	197(7)	519(64)
Cr ¹⁸ O ¹⁸ O		1076(13)	191(7)	517(63)

TABLE II. Calculated geometries, frequencies (cm^{-1}), and intensities (km/mol) for CrO₂ isomers.

^aTriplet CrOO converged to triplet $Cr(O_2)$.

diatomic isotopic ratio and doublet isotopic structure.²¹ In addition, a stronger 846.5 cm⁻¹ band was observed in the $Cr+CO_2$ reaction.

CrO₂

Sharp bands at 965.4 and 914.4 cm^{-1} appeared on deposition, increased on photolysis and decreased on annealing; additional weak satellite features at 962.4 and 959.5 cm⁻¹ and at 913.3 and 912.2 cm⁻¹ were observed. The observed intensity distribution (35:4:1) and frequency shifts are suitable for natural abundance Cr isotopes (⁵²Cr, 83.8%; ⁵³Cr, 9.6%; ⁵⁴Cr, 2.4%). Chromium isotopic structures were also detected for the corresponding oxygen isotopic bands (Fig. 3). This observation clearly identifies a molecule containing one chromium atom. The large 52/53 (1.00312) and 52/54 (1.00615) isotopic ratios for the 965.4 cm⁻¹ band are indicative of an antisymmetric vibration whereas the small 52/53 (1.00120) and 52/54 (1.00241) ratios for the 914.4 cm⁻¹ band are appropriate for the symmetric vibration. Experiments with scrambled isotopic oxygen revealed triplet isotopic structures for each band with opposite asymmetries in the positions of the ¹⁶OCr¹⁸O bands and 16/18 ratios of 1.0390 and 1.0514, respectively, for the dominant chromium isotope. The isotopic ratios show that these bands are due to antisymmetric and symmetric stretching modes of a C_{2v} molecule. The matching asymmetries (the ¹⁶OCr¹⁸O mode is 6.3 cm⁻¹ higher in the strong " ν_3 " band and 6.4 cm⁻¹ lower in the weaker " ν_1 " band due to interaction between these two modes with lower symmetry) further associate these two bands with the same molecule. Thus, these bands are assigned to the ν_3 and ν_1 stretching vibrations of the bent OCrO molecule.

The sharp oxygen and chromium isotopic bands for the ν_3 fundamental, which is alone in its symmetry class, provide a basis for calculation of the OCrO valence angle.^{15,22,23} The 16/18 ratios for ⁵²CrO₂ and ⁵³CrO₂ give 131.8° and 132.0° upper limits and the 52/53 ratios for Cr¹⁶O₂ and Cr¹⁸O₂ give 126.0° and 124.9° lower limits. These bands are sharp (FWHM=0.6 cm⁻¹) and the frequency accuracy (±0.1 cm⁻¹) introduces only ±2° of uncertainty. The average of these limits cancels anharmonic effects²² and predicts a 128°±4° valence angle for OCrO.

The bands assigned to CrO_2 in the $\text{Cr}(\text{CO})_6+5\% \text{ O}_2$ photolysis experiments¹³ must be interpreted as CrO_2 perturbed by one or more O_2 or CO molecules present in the matrix. The 969.8 cm⁻¹ band assigned by Almond¹³ to ν_3 of CrO_2 is in fact close to the present 971.4 cm⁻¹ band that grows on annealing and is probably due to the OOCrO₂ complex; the 960.2 cm⁻¹ band assigned by Almond to ν_1 of CrO_2 was not observed here. As the present work shows, natural chromium isotopic splittings can be resolved for the isolated OCrO molecule.

DFT calculations support the present assignments to OCrO stretching modes. The calculated spectra and the relative band intensities are in excellent agreement: the observed $I(\nu_1)/I(\nu_3) = 1/11$, calculated = 1/13, and the ν_1 and ν_3 frequency "scale factors" observed/calculated are 0.892 and 0.901. The experimental angle $(128^{\circ} \pm 4^{\circ})$ is in agreement with the calculated (125°) value. Finally, the calculated 16/18 isotopic ratios for ν_1 and ν_3 are 1.0513 and 1.0398, almost the same as the observed ratios.

The yield of OCrO after deposition was sufficiently high that a sharp new 1869.7 cm^{-1} band was observed with 2% of

the absorbance at 965.4 cm⁻¹. This band is 10.1 cm⁻¹ less than the sum of ν_1 and ν_3 for OCrO. It produced an almost symmetrical triplet with scrambled oxygen, and its 16/18 isotopic ratio (1.0447) is the average of the ν_1 and ν_3 isotopic ratios. Taking into account anharmonicity, the weak 1869.7 cm⁻¹ band is assigned to the $\nu_1 + \nu_3$ combination band. Note that the ${}^{52}\text{Cr}{}^{16}\text{O}_2 - {}^{53}\text{Cr}{}^{16}\text{O}_2$ isotopic splitting in the $\nu_1 + \nu_3$ band, 4.1 cm⁻¹, is the sum of these splittings, 3.0 and 1.1 cm⁻¹, in the ν_3 and ν_1 bands; similar agreement is found for Cr¹⁸O₂. Observation of this combination band confirms that the present ν_1 and ν_3 assignments are correct. Similar $\nu_1 + \nu_3$ combination bands have been observed for the OCoO, OPbO and OVO molecules.^{17,24,25}

Experiments with N₂O produced the 973.7, 970.5, and 965.4 cm⁻¹ bands on deposition. The first band increased markedly on annealing; the second and third bands increased on initial then decreased on further annealing, Experiments with O_2/N_2 mixture and its oxygen isotopic modifications revealed strong 976.3 and 973.3 cm⁻¹ bands after deposition. First annealing decreased the 976.3 and increased the 973.3 cm⁻¹ bands. Experiments with mechanical mixtures revealed doublets for each band and 16/18 isotopic ratios near 1.0386. The latter bands produced triplets with scrambled oxygen, indicating two equivalent oxygen atoms. These bands are assigned to $(N_2)_x$ CrO₂ complexes.

CrOO

Spectra in the $1200-1000 \text{ cm}^{-1}$ region are shown in Fig. 2. Three bands at 1153.9, 1134.2, and 1108.7 cm^{-1} appeared in the spectra after annealing to 25 K. Further annealing increased the first two bands and decreased the last band. The second band has been assigned to the OOCrOO molecule.⁸ The 1108.7 cm⁻¹ band revealed 1125 and 1056 cm⁻¹ components in the ${}^{16}O_2 + {}^{18}O_2$ experiments, which is analogous to the pattern for the 1134.2 cm^{-1} band. However, the 1153.9 cm^{-1} band which shifted to 1090.6 cm^{-1} with ${}^{18}\text{O}_2$, showed no intermediate with ${}^{16}\text{O}_2 + {}^{18}\text{O}_2$, and a single intermediate at 1121.1 cm⁻¹ with scrambled oxygen. The 1153.9 cm⁻¹ band is here assigned to the $Cr+O_2$ complex, but the structure [CrOO vs $Cr(O_2)$] cannot be determined. Such a complex has been proposed for reaction of ground state Cr atoms with O2 at room temperature.²⁶ DFT calculations show that the most stable Cr(O₂) state, the quintet should have an O-O vibration below 1000 cm⁻¹, which makes it similar to the analogous cyclic peroxo complexes in the Fe, Co, and Ni+O2 systems.^{14–17} On the other hand, the next $Cr(O_2)$ state, the triplet, has a calculated frequency of 1189 cm⁻¹. It is known that the $3d^5$ configuration of Cr⁺ is energetically favorable, which suggests that chromium is unlikely to transfer two electrons to O_2 to form a peroxo complex. DFT calculations suggest that quintet is the most stable state for the endbonded superoxo isomer, and a strong 1165 cm^{-1} band is predicted, which correlates with the present assignment. The question about the relative stability of CrOO and Cr(O2) remains open, and a higher level of theory must be applied to answer it.

The weak 844.8 cm⁻¹ band shifts to 800.1 cm⁻¹ with ${}^{18}O_2$, gives only these bands with the mechanical mixture and a quartet of nearly equal components with the statistical mixture. The 16/18 ratio (1.0559) characterizes an O–O stretching mode. As one chromium atom appears to be incapable of transferring two electrons to form the peroxide, expected in this region, perhaps Cr₂ can do so. The 844.8 cm⁻¹ band is tentatively assigned to such a Cr₂–OO complex with the Cr₂ arrangement undetermined but with an end-on arrangement of OO, as indicated by the quartet splitting pattern observed in experiments with scrambled O₂.

The dioxide OCrO is known from high-temperature mass spectrometric studies, and its formation from O_2 is highly exothermic.²⁷ However, the 965.4 and 914.4 cm⁻¹ bands decreased upon annealing, which means that the insertion reaction requires significant activation energy. The dioxide OCrO can be formed by reaction (3) on the matrix surface during deposition or through photolysis with energetic Cr atoms. Cold reaction (4) produces the CrOO molecule, as proposed for the room temperature process.²⁶

$$\operatorname{Cr}^* + \operatorname{O}_2 \rightarrow \operatorname{OCrO}(\Delta E = -113 \pm 11 \text{ kcal/mol}),^{27}$$
 (3)

$$Cr+O_2 \rightarrow CrOO$$
 (4)

CrO₃

The sharp 968.4 cm^{-1} band appeared in the spectra after annealing and was stronger with 1% than with 0.5% O₂. Isotopic substitution with both mixtures revealed four bands at 968.4, 960.2, 950.7, and 932.1 cm⁻¹ that increased together on annealing to 40 K with an intensity distribution of approximately 2:1:1:2, and the (16/18) isotopic ratio 1.0391 (slashes in Fig. 4(b) separate absorbance increase at these frequencies on 40 K annealing from absorbance present before annealing). This isotopic pattern is characteristic of the $\nu_3(e)$ fundamental for C_{3v} or D_{3h} XY₃ molecules, where the nondegenerate antisymmetric stretching vibrations of mixed isotopic molecules of lower symmetry also make contributions to the absorptions due to the degenerate vibration of the pure isotopic molecules,²⁸ and assignment to CrO₃ is suggested. The harmonic 16/18 isotopic ratio for the D_{3h} structure (1.404) is slightly higher than the observed value, which may be accounted for by anharmonicity. Although the $\nu_1(a_1)$ vibrations of the mixed isotopic molecules of lower symmetry are allowed, they are too weak to detect here.

The yield of CrO_3 increased on annealing: two reactions (5) and (6) are expected to be highly exothermic²⁷ and to require little activation energy. The 968.4 cm⁻¹ band was observed after deposition and markedly increased on annealing in the Cr+N₂O/Ar system. This suggests that reaction (7) is exothermic²⁷ and leads to CrO₃ formation in this system

$$CrO+O_2 \rightarrow CrO_3$$
, (5)

$$OCrO+O \rightarrow CrO_3,$$
 (6)

$$OCrO + N_2O \rightarrow CrO_3 + N_2. \tag{7}$$

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Cr(OO)₂

The 1153.9 and 1134.2 cm⁻¹ bands appeared in the spectra on annealing and grew markedly with increasing temperature. The first band increased relatively more, and the second band was always accompanied by two weak absorptions at 1137.8 and 1126.7 cm⁻¹. Both bands were observed previously, together with a weak 971.5 cm⁻¹ band. Only the 1134.2 cm⁻¹ band produced isotopic shifts, and it was assigned to the antisymmetric O–O vibration of the C_{2h} planar OOCrOO molecule.⁸

Our experiments found the same isotopic structure reported previously.⁸ In experiments with a mechanical mixture, two new counterparts at 1145.3 and 1078.5 cm⁻¹ are due to symmetric and antisymmetric vibrations of the isotopically mixed ¹⁶O¹⁶OCr¹⁸O¹⁸O molecule; the symmetric vibration is allowed due to the lowering of symmetry. Scrambled oxygen experiments produced four additional bands, namely 1114.8, 1109.8, 1103.2, and 1096.1 cm⁻¹. The complete isotopic structure cannot be resolved due to band overlap; however, seven bands from 1134.2 to 1070.8 cm⁻¹ approximate the octet required for the OOCrOO molecule with equivalent OO subunits but non-equivalent atomic orientations. The present observations agree with the previous assignment.⁸

OOCrO₂

The weak 971.4 cm⁻¹ band increased on annealing, decreased on photolysis, and produced a doublet with the mechanical mixture, but its intermediate counterpart was not detected in scrambled oxygen experiments due to band overlap. The (16/18) isotopic ratio 1.0394 is very close to that for the antisymmetric vibration of the OCrO molecule. The 971.4 cm⁻¹ band is assigned to the OOCrO₂ molecule. Although it is difficult to distinguish between side- and endbonded coordination of oxygen, the end-bonded arrangement is favored. In the V+O₂ system, a terminal O–O vibration was observed for the OOVO₂ molecule,²⁵ hence this arrangement has precedent. Note also that assignment of the 971.4 cm⁻¹ band to the antisymmetric vibration of an OCrO fragment is in a good agreement with bands observed previously in oxygen-rich matrix systems.^{11–13}

On the other hand, a sharp 973.7 cm⁻¹ band, produced on deposition and increased by photolysis, decreased on annealing. The 16/18 ratio (1.0394) is essentially the same as CrO_2 . It is suggested that the 973.7 cm⁻¹ band is also due to OOCrO₂ with a different structural arrangement of the complexing dioxygen.

CrOCr

A weak, broad 804 cm^{-1} band was produced by deposition and decreased on annealing. It was also enhanced in the Cr+N₂O system. The 804 cm^{-1} band produced doublets with mechanical mixture and scrambled oxygen with a (16/18) isotopic ratio of 1.0510. This band can be tentatively

assigned to the antisymmetric vibration of the CrOCr molecule. Estimation of valence angle lower limit from the oxygen isotopic shift gives a value of 138°.

CrOCrO

The 984.3 cm⁻¹ band was observed after deposition and increased on annealing. Oxygen isotopic substitution revealed 1:2:1 triplets with both mechanical and statistical mixtures and a (16/18) isotopic ratio of 1.0436. This isotopic ratio is half way between the diatomic ratio and that of the antisymmetric vibration of OCrO. The triplet isotopic structure in experiments with a mechanical mixture indicates the involvement of two precursor molecules in the reaction; namely, two CrO molecules. Two weak features at 983.0 and 981.8 cm⁻¹ always accompanied this band. Their ¹⁸O counterparts at 941.9 and 940.7 produced (16/18) ratios of 1.0436 and 1.0437, respectively. The intensity distribution of 17:4:1 is suitable for a molecule containing two chromium atoms, for which only (52-52), (52-53), (52-54) components can be observed. Note also that the ratios (983.4/983.0=1.00132)and 984.3/981.8=1.002 55) are significantly less than those observed for ν_3 of OCrO or the harmonic diatomic ratio 1.002 23 (52/53) and 1.004 39 (52/54), respectively, which again confirms the involvement of two chromium atoms. These bands are assigned to isotopic CrOCrO molecules. Normally a quartet oxygen isotopic structure should be observed in this case, but the intermediate band at 954.8 cm^{-1} reveals considerable asymmetry. A 1007.7 cm⁻¹ band is also observed, which is due to the "symmetric" mode of the mixed isotopic molecules. The Cr-16-Cr-18 and Cr-18-Cr-16 isotopic molecules are not resolved here; a similar pattern was found for the AlOAlO molecule.¹⁹

(Cr₂O₂)

The bands from 761 cm⁻¹ to lower frequencies are probably too low to be due to terminal Cr–O vibrations, hence bridge-bonded species must be considered. The CaO molecule (746.7 cm⁻¹) forms a rhombic dimer (Ca₂O₂) absorbing at 584.6 and 516.3 cm⁻¹.²⁹ The sharp 716.2, 700.8, and 643.1 cm⁻¹ bands reveal higher multiplets with the statistical mixture, but the 628.2 cm⁻¹ band gives a triplet for the vibration of two equivalent oxygen atoms. If this band is due to cyclic (Cr₂O₂), the ring may be puckered since the 16/18 ratio is lower than the "diatomic" value required for the D_{2h} structure. The 628.2 cm⁻¹ band is tentatively assigned to a cyclic, nonplanar (Cr₂O₂) molecule, where puckering may be caused by Cr–Cr bonding across the ring.

The observation of CrOCrO after deposition and cyclic Cr_2O_2 only after annealing suggests different mechanisms for their formation. In experiments with isotopic mixtures, triplets were observed in the former case and doublet and triplet structures in the latter. It appears that the dimerization reaction yields only CrOCrO and the addition of a second Cr to OCrO yields cyclic (Cr₂O₂).

Cr_2O_4

The sharp 716.2 cm^{-1} band was observed on deposition, increased on annealing to 25 K, and decreased slightly with further annealing. Oxygen isotopic substitution revealed asymmetric triplet isotopic structures with both mechanical and statistical mixtures. The mechanical mixture gave a sharp triplet at 716.2, 711.4, and 686.8 cm^{-1} , with first and last components identical to pure isotopic values, and a 16/18 ratio of 1.0428, which is appropriate for an antisymmetric mode. The statistical mixture, however, gave a broadened triplet at 715.9, 711.4, and 687.0 cm^{-1} , which is actually a triplet of unresolved triplets when examined on expanded wave number scale. The 716.2 cm⁻¹ band was always accompanied by two weak features at 715.3 and 714.4 cm^{-1} , and the intensity distribution of these bands was close to 17:4:1, as in the previous case of the OCrOCr molecule. Furthermore, the 52/53 and 52/54 ratios (1.001 26 and 1.002 52) are very close to those just described above. Thus, based on isotopic results, this product contains two chromium atoms and at least two oxygen atoms.

The sharp 643.1 cm⁻¹ band tracks with the 716.2 cm⁻¹ band to better than 10% on annealing in all of these experiments. The 643.1 cm⁻¹ band produced a sharp primary triplet at 643.1, 627.7, and 611.4 cm⁻¹ with the mechanical mixture and a resolved nonet (or triplet of triplets) with the statistical mixture (Fig. 5). This clearly identifies a product with four oxygen atoms containing two different pairs but equivalent atomic positions in each pair. The 16/18 ratio 1.0519 is appropriate for a symmetric motion. Thus we have identified from 716.2 and 643.1 cm⁻¹ bands a molecule with two equivalent Cr atoms and two nonequivalent sets of two equivalent O atoms.

The appearance of the 716.2 and 643.1 cm^{-1} bands on deposition with the major OCrO product and their parallel annealing behavior suggests that the above bands are due to $(CrO_2)_2$ as demonstrated by the spectrum in Fig. 5(c). The resolution of Cr isotopic splittings on the 716.2 cm⁻¹ band, an antisymmetric mode more dependent on Cr, and O isotopic splittings on the 643.1 cm^{-1} absorption, a symmetric mode more dependent on O, clearly identifies this molecule. Two structures must be considered: an ethylene-like arrangement with Cr-Cr bonding and a O(Cr₂O₂)O puckered ring with terminal O atoms. That the 716.2 and 643.1 cm^{-1} bands are 249–271 cm⁻¹ below the ν_3 and ν_1 modes for isolated OCrO vibrations strongly suggests the ring structure. The isotopic ratio 1.0428 and 1.0519 separations from the diatomic 16/18 value (1.0453) indicates the nonplanar or puckered nature of this ring. Note that the puckered ring may also involve Cr-Cr bonding.

Cr₂O₃

The weak band at 700.8 cm⁻¹ was observed after annealing. In experiments with both mixed and scrambled isotopic oxygen samples a triplet of doublets was observed. The (16/18) isotopic ratio of 1.0497 is very close to that of the symmetric ring vibration of $O(Cr_2O_2)O$. The isotopic structures are appropriate for interaction between two equivalent The 1044.8 cm⁻¹ band also appears on annealing but this band is in the terminal Cr–O stretching region. Mixed oxygen isotopic experiments show the participation of at least two, and possibly more, oxygen atoms. The best assignment of this band is to the bent OCrOCrO molecule, but without completely resolved isotopic spectra, this identification is not definitive. Analogous Ni₂O₃ and Cu₂O₃ molecules have been found in this frequency region.^{16,30} The annealing behavior suggests the following association mechanism of formation:

$$OCr+OCrO \rightarrow OCrOCrO$$
 and $(Cr_2O_2)O$. (8)

The dimerization of chromium dioxide molecules proceeds on deposition and on annealing

$$2OCrO \rightarrow O(Cr_2O_2)O. \tag{9}$$

Other absorptions

Several weak absorptions cannot be identified from the present observations; these are due to minor species and indicated by Cr_xO_y in Table I. Although CrO_2^- is expected to be stable,³¹ we have no spectroscopic evidence for this molecular anion. In this regard only a trace of O_4^- was observed at 953.8 cm⁻¹ in these experiments.^{23,24,32}

CONCLUSIONS

Pulsed laser-evaporated chromium atoms react with oxygen to produce CrO and OCrO, which are trapped in solid argon. Chromium dioxide is characterized here from sharp ν_1 and ν_3 fundamentals and the $\nu_1 + \nu_3$ combination band all with triplet mixed oxygen isotopic absorptions and resolved natural chromium isotopic splittings; this isotopic data provides a 128°±4° valence angle measurement. Further association of reagents and the primary products in the matrix leads to the formation of the CrOO, CrO_3 , OOCrOO, Cr_2O_2 , Cr_2O_3 , and Cr_2O_4 molecules, which are also identified by oxygen and chromium isotopic shifts and splittings. Although formation of the insertion product is exothermic, annealing behavior does not show evidence of a cold reaction. This means that formation of OCrO requires substantial activation energy and complexes of Cr and oxygen do not undergo further reaction. Among other possible isomers of chromium dioxide only the CrOO molecule was found.

Two isomeric forms are proposed for Cr_2O_2 , the asymmetric bent CrOCrO molecule, and the symmetrical puckered ring (Cr_2O_2). It is interesting that the dimerization of CrO leads to formation of the first isomer, while the ring molecule is formed from the reaction of CrO_2 with Cr on annealing. Likewise, evidence is found for two isomers of Cr_2O_3 , a bent OCrOCrO molecule and a puckered ring with

one terminal oxygen atom, $(Cr_2O_2)O$. Finally, $(CrO_2)_2$ is definitively identified from resolved chromium and oxygen isotopic splittings, and a puckered ring structure with two terminal oxygen atoms is proposed, namely $O(Cr_2O_2)O$. These rings may be puckered by Cr–Cr bonding across the ring.

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