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Matrix Isolation Infrared Spectroscopic and Theoretical Study of Dinuclear Chromium Oxide Clusters: Cr_2O_n ($n = 2, 4, 6$) in Solid Argon

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Dichromium oxide clusters, Cr_2O_2, Cr_2O_4, and Cr_2O_6, have been prepared and characterized by matrix isolation infrared spectroscopy and quantum chemical calculations. Laser-evaporated chromium atoms reacted with O_2 in solid argon to form the previously characterized CrO_2 molecules, which further reacted with chromium atoms to form Cr_2O_2 spontaneously on annealing. The Cr_2O_2 cluster is determined to have a chainlike CrOCrO structure. The rhombic ring isomer, which was predicted to be more stable than the CrOCrO structure, was not formed at the present experimental conditions. The Cr_2O_4 cluster was formed from the barrierless dimerization of the chromium dioxide molecules, which is characterized to have a planar D_{2h} symmetry. TheCr_2O_6 cluster was produced under UV light irradiation. It is determined to have a singlet ground state with a nonplanar D_{2h} symmetry.

Introduction

Chromium oxides are widely used as catalysts in many important industrial processes.[1] The simple metal oxide clusters serve as model systems to obtain molecular-level information for surface and catalytic processes. The chromium monoxide molecule has been well studied in the gas phase.[2,3] The investigations on the reactions of chromium atoms and oxygen molecules as well as the photooxidation of $Cr(CO)_6$ in oxygen-rich matrixes have characterized the bent dioxide molecule and some other chromium oxide complexes.[4−6] The electronic structure of CrO_n^- and CrO_n ($n = 1-5$) was also studied using anion photoelectron spectroscopy and density functional theory calculations.[7] The electron affinities, vibrational, and electronic structure information about the CrO_n neutrals were obtained. Recently, the dichromium oxide clusters have received particular attention. Density functional theory (DFT) calculations have been performed by Reddy and co-workers to predict the electronic structures of the Cr_2O_n ($n = 1-6$) clusters and to investigate the effect of chemical composition on the magnetic behavior.[8,9] It was shown that the magnetic coupling between the chromium sites oscillates as a function of *n*. Pandey et al. also reported DFT calculations on the vibrational frequencies of the Cr_2O_n ($n = 1-4$) clusters to provide a description of the observed infrared absorptions from the reactions of laser-ablated chromium atoms with dioxygen in solid argon matrix.[10,11] Both the linear and the ringlike isomers were predicted to be equally probable for Cr_2O_2, while the ringlike isomer is preferred over the chainlike isomer for Cr_2O_3. For Cr_2O_4, the $O(Cr_2O_2)O$ isomer is preferred over the $(CrO_2)_2$ isomer. The equilibrium geometry and electron detachment energies of $Cr_2O_n^-$ ($n = 4-6$) cluster anions were also theoretically predicted.[12] Experimentally, a photoelectron spectroscopic study on $Cr_2O_n^-$ ($n = 1-3$) was first reported by Kondow and co-workers.[13,14] More recently, a systematic photoelectron spectroscopic study on $Cr_2O_n^-$ with $n = 1-7$ was performed by Wang and co-workers.[15] Well-resolved PES spectra were obtained for each cluster at different photon energies. In this Article, the reactions of chromium atoms with dioxygen were reinvestigated. Dichromium oxide clusters, Cr_2O_n ($n = 2, 4, 6$), were prepared and studied to provide vibrational frequencies and further understanding of the structure and bonding properties of these clusters. We will show that the absorption previously assigned to CrOCrO is due to the stretch mode of Cr_2O_4, and new assignment on CrOCrO will be made via different O_2 concentration and laser power experiments together with isotopic substitution and density functional theory calculations. In addition, the Cr_2O_6 cluster is also identified.

Experimental and Theoretical Methods

The experimental setup for pulsed laser evaporation and matrix isolation infrared absorption spectroscopic investigation has been described in detail previously.[16] Briefly, a Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating chromium metal target through a hole in a CsI window. The laser-evaporated chromium atoms were co-deposited with O_2 in excess argon onto the 6 K CsI window. The CsI window was mounted on a copper holder at the cold end of the cryostat and maintained by a closed-cycle helium refrigerator (ARS, 202N). In general, matrix samples were deposited for 1−2 h with a gas deposition rate of approximately 4 mmol per hour. After sample deposition, IR spectra were recorded on a Bruker IFS66V spectrometer at 0.5 cm^{-1} resolution using a liquid nitrogen cooled HgCdTe (MCT) detector for the spectral range of 4000−450 cm^{-1}. Samples were annealed at different temperatures and subjected to broad-band irradiation using a high-pressure mercury arc lamp with glass filters.

Quantum chemical calculations were performed to predict the structures and vibrational frequencies of the reaction products using the Gaussian 03 program.[17] Calculations were performed using the Becke's three-parameter hybrid functional with the Lee−Yang−Parr correlation corrections (B3LYP).[18] The 6-311+G(d) basis set was used for the O atom, and the all-electron basis set of Wachters−Hay as modified by Gaussian

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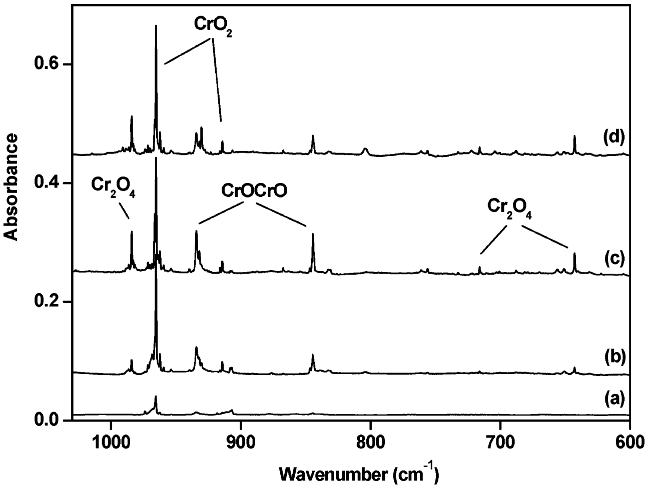


Figure 1. Infrared spectra in the 1030−600 cm^{-1} region from co-deposition of laser-evaporated Cr atoms with 0.05% O_2 in argon: (a) 1 h of sample deposition at 6 K, (b) after annealing to 25 K, (c) after annealing to 35 K, and (d) after 15 min broad-band irradiation ($250 < \lambda < 580$ nm).

was used for the Cr atom.[19] The geometries were fully optimized; the harmonic vibrational frequencies were calculated, and zero-point vibrational energies (ZPVE) were derived.

Results and Discussion

Infrared Spectra. The infrared spectra of laser-evaporated chromium atoms co-deposited with 0.05% O_2 in argon using relatively high laser power (10 mJ/pulse) are shown in Figure 1 in the 1030−600 cm^{-1} region. After 1 h of sample deposition at 6 K (Figure 1, trace a), absorptions of chromium dioxide at 965.3 (ν_3) and 914.3 cm^{-1} (ν_1) were observed,[6] which increased markedly upon sample annealing to 25 K (Figure 1, trace b). Product absorptions at 984.1, 934.4, 844.6, 716.1, and 642.9 cm^{-1} were produced upon 25 K annealing. On the basis of their growth/decay characteristics measured as a function of experimental conditions, these new product absorptions can be classified into two groups. As shown in Figure 1, the 934.4 and 844.6 cm^{-1} absorptions can be grouped together, which markedly increased upon sample annealing to 35 K, but decreased under broad-band irradiation. The 984.1, 716.1, and 642.9 cm^{-1} absorptions are due to different vibrational modes of the same species. These three absorptions increased together upon 35 K annealing and remained almost unchanged upon broad-band irradiation. It is noteworthy that the CrO absorption at 846.3 cm^{-1} was not detected throughout the experiment.[6]

Experiments with different O_2 concentrations were performed. Figure 2 shows the spectra in the 1050−600 cm^{-1} region with 0.25% O_2 in argon using the same laser power as in Figure 1. The CrO_2 absorptions are strong after sample deposition; weak O_4^- absorption at 953.8 cm^{-1},[20] and CrO and CrO_3 absorptions at 846.3 and 968.4 cm^{-1} were also observed.[6] The 984.1, 716.1, and 642.9 cm^{-1} absorptions were produced on sample deposition, increased on 25 K annealing, and remained almost unchanged upon subsequent 35 K annealing and broad-band irradiation. The 934.4 and 844.6 cm^{-1} absorptions were barely observed upon sample annealing. By contrast, a group of new absorptions at 1014.8, 975.4, 704.1, and 690.5 cm^{-1} was produced under broad-band irradiation.

The experiments were repeated by using the isotopic-labeled $^{18}O_2$ sample and the $^{16}O_2 + {}^{18}O_2$ and $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ mixtures. The spectra in selected regions with different isotopic samples are shown in Figures 3−5, respectively. The band positions of the new product absorptions are summarized in Table 1.

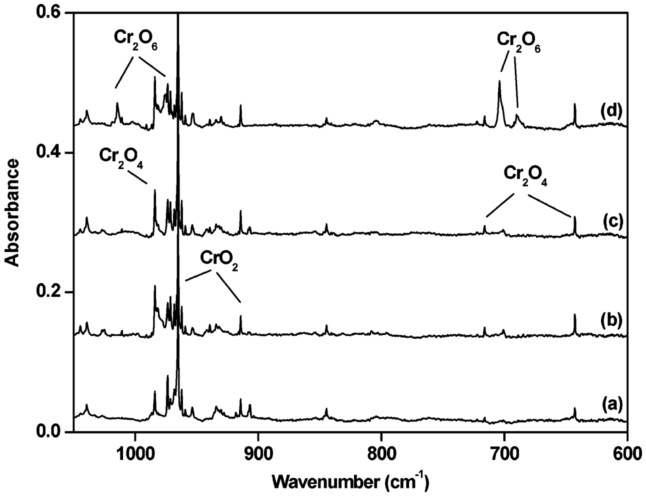


Figure 2. Infrared spectra in the 1050−600 cm^{-1} region from co-deposition of laser-evaporated Cr atoms with 0.2% O_2 in argon: (a) 1 h of sample deposition at 6 K, (b) after annealing to 25 K, (c) after annealing to 35 K, and (d) after 15 min broad-band irradiation ($300 < \lambda < 580$ nm).

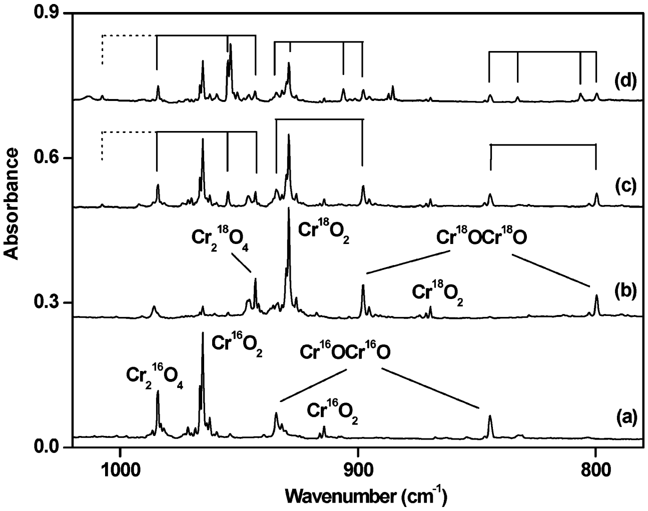


Figure 3. Infrared spectra in the 1020−780 cm^{-1} region from co-deposition of laser-evaporated Cr atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing: (a) 0.1% $^{16}O_2$, (b) 0.1% $^{18}O_2$, (c) 0.05% $^{16}O_2$ + 0.05% $^{18}O_2$, and (d) 0.025% $^{16}O_2$ + 0.05% $^{16}O^{18}O$ + 0.025% $^{18}O_2$.

CrOCrO. The absorptions at 934.4 and 844.6 cm^{-1} were only observed in the experiments with low O_2 concentrations. The upper band shifted to 897.8 cm^{-1} with $^{18}O_2$. The $^{16}O/^{18}O$ isotopic frequency ratio of 1.0408 is slightly higher than that of the antisymmetric stretching mode of the bent CrO_2 molecule (1.0394). The low mode shifted to 799.6 cm^{-1} with $^{18}O_2$. The $^{16}O/^{18}O$ isotopic frequency ratio of 1.0563 is also higher than that of the symmetric stretching mode of CrO_2 (1.0514). For both modes, only the pure isotopic counterparts were observed in the experiment with equal molar mixture of $^{16}O_2$ and $^{18}O_2$ (Figure 3, trace c). In the experiment with the $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ (1:2:1) sample, four absorptions at 844.6, 832.9, 806.5, and 799.6 cm^{-1} with approximately equal IR intensities were resolved for the low mode. The upper mode should also split into four absorptions with two intermediate absorptions: one observed at 906.1 cm^{-1} and another one being overlapped by the strong $Cr^{18}O_2$ absorption at 929.2 cm^{-1}. These spectral

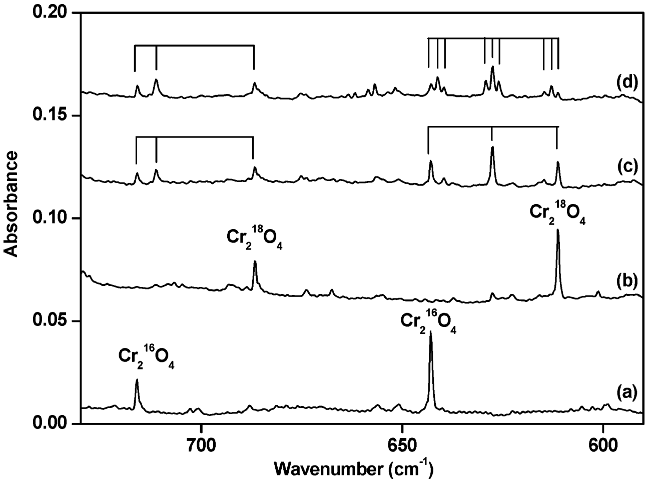


Figure 4. Infrared spectra in the 730−590 cm^{-1} region from co-deposition of laser-evaporated Cr atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing: (a) 0.1% $^{16}O_2$, (b) 0.1% $^{18}O_2$, (c) 0.05% $^{16}O_2$ + 0.05%$^{18}O_2$, and (d) 0.025% $^{16}O_2$ + 0.05% $^{16}O^{18}O$ + 0.025% $^{18}O_2$.

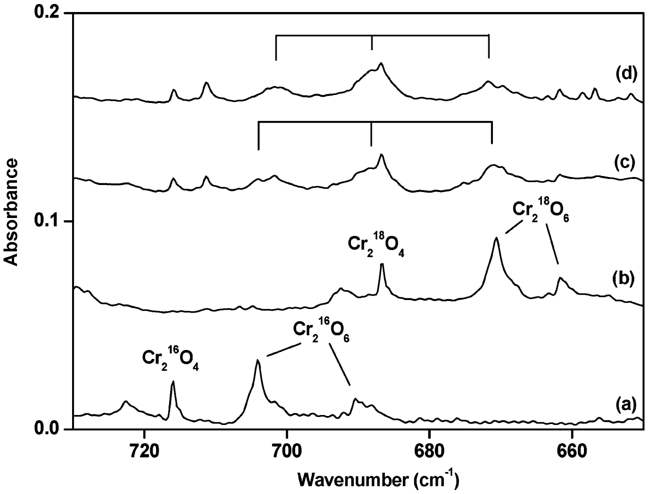


Figure 5. Infrared spectra in the 730−650 cm^{-1} region from co-deposition of laser-evaporated Cr atoms with isotopic-labeled O_2 in excess argon. Spectra were taken after 1 h of sample deposition at 6 K followed by 35 K annealing and 15 min broad-band irradiation: (a) 0.1% $^{16}O_2$, (b) 0.1% $^{18}O_2$, (c) 0.05% $^{16}O_2$ + 0.05%$^{18}O_2$, and (d) 0.025% $^{16}O_2$ + 0.05% $^{16}O^{18}O$ + 0.025% $^{18}O_2$.

features indicate that these product absorptions involve two inequivalent oxygen atoms, which arise from one dioxygen molecule. Accordingly, we assign the 934.4 and 844.6 cm^{-1} absorptions to a CrOCrO molecule. In the previous matrix isolation study,[6] a 984.3 cm^{-1} absorption was assigned to the CrOCrO molecule. As will be discussed below, this absorption should be assigned to the Cr_2O_4 cluster.

The geometry and electronic structure of Cr_2O_2 has been the subject of several previous theoretical investigations.[8−11] Two structural isomers, a linear chainlike CrOCrO structure and a rhombic cyclic structure, were predicted to be stable isomers. These two structural isomers were predicted to be quite close in energy with the cyclic one slightly more stable than the linear structure. We performed geometry optimization and vibrational frequency calculations on these two structures at the DFT/B3LYP level of theory. The optimized structures are shown in Figure 6. Both the chainlike and the cyclic structures were predicted to have a nonet ground state. The chainlike structure was predicted to be bent with ∠CrOCr and ∠OCrO of 158.7° and 145.4°, respectively. The linear structure was predicted to be a transition state with one imaginary frequency. The bent CrOCrO structure was computed to be 6.4 kcal/mol higher in energy than the cyclic isomer at the DFT/B3LYP level of theory. As listed in Tables 2and 3, the two experimentally observed modes were calculated at 966.4 (400 km/mol) and 832.3 cm^{-1} (462 km/mol), with the isotopic frequency ratios also matching the experimental values. All other modes were predicted to have frequencies below 400 cm^{-1} and were not observed. The cyclic Cr_2O_2 isomer was predicted to have two strong ring puckering vibrations at 619.6 (202 km/mol) and 594.5 cm^{-1} (404 km/mol) (Table 2). No obvious absorptions were observed in this frequency region in present experiments. A 628.2 cm^{-1} absorption has tentatively been assigned to the cyclic cluster in the previous matrix isolation study.[6] Population analysis indicates that the spin densities of the $^9A''$ ground state of CrOCrO are mainly distributed at the two chromium centers, and hence the Lewis structure can be drawn as:

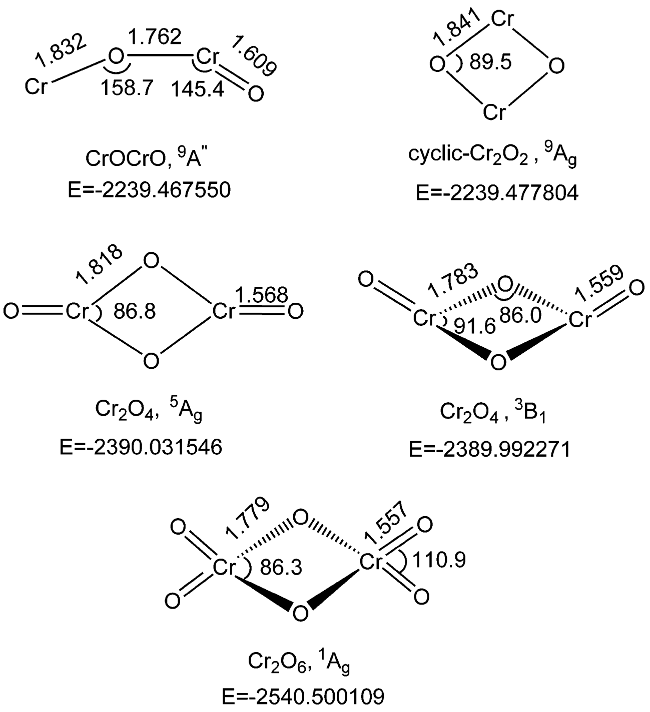
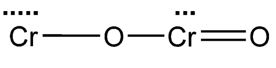


Figure 6. Optimized structures (bond lengths in angstrom, bond angles in degree) for the Cr_2O_n (n = 2, 4, 6) clusters.



Cr_2O_4. The 984.1, 716.1, and 642.9 cm^{-1} absorptions correspond to the absorptions reported at 984.3, 716.2, and 643.1 cm^{-1} that were previously assigned to the CrOCrO and Cr_2O_4 absorptions.[6] The present experimental observations indicate that these three absorptions exhibited constant relative IR intensities throughout all of the experiments, implying that these absorptions are due to different vibrational modes of the same species. In agreement with a previous report,[6] the 716.1 cm^{-1} absorption splits into a sharp triplet at 716.1, 711.4, and 686.7 cm^{-1} when the equal molar mixture of $^{16}O_2$ and $^{18}O_2$ was used (Figure 4, trace c). When the $^{16}O_2$ + $^{16}O^{18}O$ + $^{18}O_2$ sample was used, a slightly broadened triplet was produced (Figure 4, trace d). The 642.9 cm^{-1} absorption also splits into a triplet at 642.9, 627.6, 611.3 cm^{-1} with the $^{16}O_2$ + $^{18}O_2$ mixture. A clearly resolved nonet or triplet of triplets (Figure 4, trace d) was identified with the $^{16}O_2$ + $^{16}O^{18}O$ + $^{18}O_2$. These spectral features indicate that two equivalent O atoms were involved in these two modes and

TABLE 1: Infrared Absorptions (cm^{-1}) from Co-deposition of Laser-Evaporated Chromium Atoms and Dioxygen in Excess Argon

$^{16}O_2$	$^{18}O_2$	$^{16}O_2 + {}^{18}O_2$	$^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$	assignment
934.4	897.8	934.4, 897.8	934.4, 928.8, 906.1, 897.8	CrOCrO
844.6	799.6	844.6, 799.6	844.6, 832.9, 806.5, 799.6	CrOCrO
986.5	945.6			$^{50}Cr^{52}CrO_4$
984.1	943.0	1007.7, 984.1, 954.6, 943.0	1007.7, 984.1, 954.6, 943.0	$^{52}Cr^{52}CrO_4$
982.9	941.8			$^{52}Cr^{53}CrO_4$
981.6	940.6			$^{52}Cr^{54}CrO_4$
716.1	686.7	716.1, 711.4, 686.7		Cr_2O_4
642.9	611.3	642.9, 627.6, 611.3	642.9, 641.2, 639.7, 629.2, 627.6, 626.0, 614.7, 612.9, 611.3	Cr_2O_4
1014.8	976.1			Cr_2O_6
975.4	936.8			Cr_2O_6
704.1	670.7	704.1, 689.7, 670.7		Cr_2O_6
690.5	661.7			Cr_2O_6

TABLE 2: Calculated Vibrational Frequencies (Unscaled Harmonic Values in cm^{-1}) and Intensities (km/mol) of the Reaction Products (Only the Frequencies above 400 cm^{-1} Are Listed)

molecule		frequency (intensity)
CrO	$^5\Pi$	867.5 (173)
CrO_2	$^3B_1$	1031.6 (488), 988.2 (23)
CrOCrO	$^9A''$	966.4 (401), 832.3 (462)
Cr_2O_2	^9A_g	671.9 (0), 619.6 (202), 594.5 (405), 463.7 (0)
Cr_2O_4	^5A_g	1070.3 (0), 1039.8 (857), 720.6 (0), 671.6 (202), 667.9 (385)
Cr_2O_6	^1A_g	1109.7 (362), 1100.9 (0), 1099.4 (0), 1067.4 (463), 767.3 (0), 731.3 (411), 706.9 (122), 471.7 (0), 466.1 (0), 400.9 (0)

were coupled by another two equivalent O atoms. The 984.1 cm^{-1} absorption lies in the region expecting for a terminal Cr$-$O stretching vibration. The mixed isotopic spectral features indicate that two equivalent O atoms are involved in this mode. As has been pointed out in a previous report,[6] two weak absorptions at 983.0 and 981.8 cm^{-1} always accompanied the 984.1 cm^{-1} absorption. The relative IR intensities among these three absorptions are approximately 17:4:1. Besides these three absorptions, a weak absorption at 986.5 cm^{-1} with IR intensity slightly higher than the 981.8 cm^{-1} absorption can also be resolved to track with the 984.1 cm^{-1} absorption. This chromium isotopic feature is appropriate for a molecule containing two equivalent chromium atoms. Accordingly, we assign the 984.1 cm^{-1} absorption to the antisymmetric Cr═O stretching mode of the Cr_2O_4 cluster. No other absorption was observed in the terminal Cr═O stretching frequency region, suggesting that the Cr_2O_4 cluster is central symmetric.

Previous DFT calculations predicted that the Cr_2O_4 cluster has a triplet ground state with a nonplanar C_{2v} symmetry having a four-membered Cr_2O_2 ring and two terminal Cr═O bonds.[8−11] Another ethylene-like structural isomer with Cr$-$Cr bonding was predicted to lie much higher in energy than the C_{2v} structure. The vibrational frequency calculation results indicate that the C_{2v} structure should have two IR-active terminal Cr═O stretching modes, which are in disagreement with the present experimental observations. Present DFT/B3LYP calculations predicted that a quintet with a planar D_{2h} symmetry (Figure 6) is the most stable structure for the Cr_2O_4 cluster. At the DFT/B3LYP level of theory, the quintet planar structure is 24.6 kcal/mol more stable than the triplet nonplanar structure. The three experimentally observed vibrational modes were computed at 1039.8, 671.6, and 667.9 cm^{-1} (Table 2). The symmetric Cr═O stretching mode of Cr_2O_4 was computed at 1070.3 cm^{-1}; this mode is IR inactive for the centrosymmetric Cr_2O_4 cluster. However, this mode of partially substituted $^{16}OCr(\mu\text{-}O)_2Cr^{18}O$ is IR active because of the reduced symmetry and was predicted at 1059.9 cm^{-1}. A weak absorption at 1007.7 cm^{-1} observed in the mixed $^{16}O_2 + {}^{18}O_2$ spectrum is due to the symmetric mode of $^{16}OCr(\mu\text{-}O)_2Cr^{18}O$. The ^5A_g ground state of Cr_2O_4 has an electron configuration of (core) $(a_u)^1(a_g)^1(b_{1u})^1(b_{1g})^1$ with the four unpaired electrons occupying the nonbonding molecular orbitals, which are largely chromium 3d in character.

Cr_2O_6. The absorptions at 1014.8, 975.4, 704.1, and 690.5 cm^{-1} were produced only under broad-band irradiation with relatively high O_2 concentrations. The 704.1 and 690.5 cm^{-1} absorptions exhibited isotopic frequency ratios that are characteristic of Cr$-$O stretching vibrations. The band positions and isotopic splittings in the mixed $^{16}O_2 + {}^{18}O_2$ and $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ experiments strongly suggest the involvement of a cyclic Cr_2O_2 subunit. The 1014.8 and 975.4 cm^{-1} absorptions lie in the region expected for terminal Cr═O stretching vibrations. Both absorptions showed antisymmetric O═Cr═O stretching vibrational ratios. These absorptions are assigned to different vibrational modes of the Cr_2O_6 cluster.

The assignment is supported by theoretical calculations. Our DFT/B3LYP calculations indicate that the Cr_2O_6 cluster has a closed-shell singlet ground state with a D_{2h} symmetry (Figure 6), in agreement with the previous calculations.[8,9,21] The four experimentally observed modes were predicted to absorb at 1109.7, 1067.4, 731.3, and 706.9 cm^{-1} with relative IR intensities in good agreement with the experimental observations (Tables 2 and 3). The W_2O_6 cluster was recently characterized to have a similar D_{2h} symmetry with a large HOMO$-$LUMO gap.[22]

Reaction Mechanism. The experimental observations clearly demonstrate that laser-evaporated chromium atoms react with dioxygen to give primarily the insertion product CrO_2. In the experiment with low O_2 concentration, the CrOCrO absorptions increased upon sample annealing. There are three possible reactions to form the CrOCrO clusters in solid argon: (i) dimerization of chromium monoxide molecules; (ii) reaction of chromium dimer with dioxygen; and (iii) reaction of chromium atom with chromium dioxide molecule. At the experimental condition of Figure 1, which favors the formation of CrOCrO, the chromium monoxide absorption was barely observed. Of more importance, the experiments with mixed $^{16}O_2 + {}^{18}O_2$ and $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ samples indicate that the two O atoms in CrOCrO come from one O_2 molecule, and hence the formation of CrOCrO from the dimerization reaction of chromium monoxide molecules can be ruled out. The reaction of chromium dimer with dioxygen also has low possibility. Recent investigations on the reactions of metal dimers with diatomic molecules such as O_2, N_2, and CO demonstrate that

TABLE 3: Comparison between the Observed and Calculated Vibrational Frequencies (cm^{-1}) and Isotopic Frequency Ratios for the Cr_2O_n (n = 2, 4, 6) Clusters

		frequency		$^{16}O/^{18}O$	
molecule	mode	obsd	calcd	obsd	calcd
CrOCrO	a'	934.4	966.4	1.0408	1.0426
	a'	844.6	832.3	1.0563	1.0543
Cr_2O_4	b_{1u}	984.1	1039.8	1.0436	1.0439
	b_{2u}	716.1	671.6	1.0428	1.0437
	b_{1u}	642.9	667.9	1.0517	1.0531
Cr_2O_6	b_{2u}	1014.8	1109.7	1.0396	1.0398
	b_{3u}	975.4	1067.4	1.0412	1.0477
	b_{3u}	704.1	731.3	1.0498	1.0492
	b_{1u}	690.5	706.9	1.0435	1.0426

all of these reactions resulted in the formation of cyclic products.[23−29] In the previous study on the reactions of laser-ablated chromium with dioxygen employing quite high laser power (40−50 mJ/pulse),[6] a 628.2 cm^{-1} absorption has been tentatively assigned to the cyclic Cr_2O_2 cluster. We suggest that the cyclic Cr_2O_2 cluster was formed by the reaction of Cr_2 and O_2, whereas the chainlike CrOCrO isomer was formed by the reaction of chromium atom with CrO_2, reaction 1, which was predicted to be exothermic by about 61.3 kcal/mol. The CrOCrO absorptions increased on sample annealing, indicating that reaction 1 requires negligible activation energy. Our DFT calculations also show that the reaction is barrierless.

$$\mathrm{Cr}\ (^7\mathrm{S}) + \mathrm{CrO_2}\ (^3\mathrm{B_1}) \rightarrow \mathrm{CrOCrO}\ (^9\mathrm{A}'') \qquad \Delta E = -61.3\ \mathrm{kcal/mol} \quad (1)$$

Although the cyclic Cr_2O_2 cluster was predicted to be more stable than the CrOCrO isomer, the cyclic Cr_2O_2 cluster was not observed in the present experiments. This suggests that the isomerization reaction from CrOCrO to cyclic Cr_2O_2 requires significant activation energy and cannot proceed under present experimental conditions.

The Cr_2O_4 clusters were produced by the dimerization reaction between two chromium dioxide molecules, reaction 2. The experimental observations indicate that this dimerization reaction proceeds spontaneously on sample annealing, which suggests that the reaction requires negligible activation energy. Consistent with experimental observation, this dimerization reaction is predicted to be barrierless and exothermic by 87.2 kcal/mol. Similar reactions have been observed in the reactions of group IVB metals with dioxygen.[29]

$$2\mathrm{CrO_2}\ (^3\mathrm{B_1}) \rightarrow \mathrm{Cr_2O_4}\ (^5\mathrm{A_g}) \qquad \Delta E = -87.2\ \mathrm{kcal/mol} \quad (2)$$

The Cr_2O_6 cluster is most likely formed by the reaction of Cr_2O_4 with dioxygen, reaction 3, which was predicted to be exothermic by 63.9 kcal/mol. As the Cr_2O_4 cluster has a quintet ground state, while the Cr_2O_6 cluster has a singlet ground state, reaction 3 requires spin crossing and may proceed via a complicated process. The Cr_2O_6 cluster absorptions were produced only under UV light irradiation, which indicates that the reaction requires activation energy, and some excited states may be involved in this photochemical process.

$$\mathrm{Cr_2O_4}\ (^5\mathrm{A_g}) + \mathrm{O_2}\ (^3\textstyle\sum_g^-) \rightarrow \mathrm{Cr_2O_6}\ (^1\mathrm{A_g}) \qquad \Delta E = -63.9\ \mathrm{kcal/mol} \quad (3)$$

Conclusions

The reactions of chromium atoms with molecular oxygen in solid argon were investigated using matrix isolation infrared absorption spectroscopy. Besides the previously characterized chromium dioxide molecule, dinuclear chromium oxide clusters, Cr_2O_2, Cr_2O_4, and Cr_2O_6, were produced and were identified on the basis of isotopic substitution and quantum chemical theoretical calculations. The Cr_2O_2 cluster was formed through the reaction of chromium atom and CrO_2 without significant activation barrier. It was characterized to have a $^9A''$ ground state with a near linear chainlike CrOCrO structure. The Cr_2O_4 cluster was formed from the dimerization of the metal dioxide molecules, which requires negligible activation energy. The Cr_2O_4 cluster was determined to have a ^5A_g ground state with a planar D_{2h} symmetry having a cyclic Cr_2O_2 subunit and two terminal Cr═O bonds. The Cr_2O_6 cluster was produced under UV light irradiation. It was predicted to have a singlet ground state with a D_{2h} symmetry.

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References and Notes

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