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Infrared, Raman, and visible spectroscopic studies of Zn and Cd matrix reactions with ozone. Spectra of metal ozonides and oxides in solid argon and nitrogen

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Reactions of zinc and cadmium atoms with ozone during condensation with excess nitrogen or argon produced $B^+O_3^-$ ion-pairs having infrared, Raman, and optical spectra similar to the analogous alkali and alkaline earth metal species. Additional infrared and Raman evidence was found for a different $B^+O_3^-$ ion-pair geometry. Mercury arc photolysis reduced ozonide absorptions and produced new 810 cm⁻¹ zinc isotopic triplets which showed the appropriate ¹⁸O shifts for ZnO, and a new 719 cm⁻¹ band which showed the proper ¹⁸O displacement for CdO. This nitrogen matrix work provides good measures of the yet-to-be-observed gas-phase fundamentals of these high temperature oxides.

INTRODUCTION

The metal atom-matrix reaction technique has proven to be a good synthetic route to high temperature oxides in infrared studies of matrix-isolated MgO, CaO, SrO, and BaO.¹⁻⁴ Since no optical spectroscopic data are available for ZnO and CdO, the corresponding ozone reactions were performed to identify the zinc and cadmium oxide molecules. The alkali and alkaline earth metal ozonide species $A^*O_3^-$ have been characterized in earlier infrared, Raman, and optical studies from this laboratory.¹⁻⁸ The group IIB zinc and cadmium studies were done, in part, to explore the effect of a higher ionization energy metal reagent on the charge-transfer $B^*O_3^-$ product species.

EXPERIMENTAL

The cryogenic and vacuum apparatus and techniques for evaporating metal atoms and preparing ozone have been described previously, 3, 7, 9-11 Briefly, zinc (Mallinckrodt) or cadmium (Fisher) atoms were evaporated from a Knudsen cell (Zn. 200-250 °C; Cd. 180-200 °C) and condensed with Ar/O_3 or $N_2/O_3 = 200/1$ mixtures on a substrate suitable for spectroscopic study. Infrared spectra of samples prepared on a 15-20 K CsI window for 20-24 h were recorded on a Beckman IR-12 spectrophotometer using expanded wavenumber scale; wavenumber accuracy is ± 0.5 cm⁻¹ in general or ± 0.2 cm⁻¹ within a single scan.^{3,9} Additional spectra of selected samples were scanned following photolysis with the light of a high pressure mercury arc (BH-6-1, Illumination Industries) filtered through water and glass filters, or following thermal cycling to 35-40 K. Visible-ultraviolet spectra were recorded on a Cary 17 spectrophotometer for samples deposited on a 20 K sapphire plate for 4-6 h.⁷ Raman spectra of similar samples, deposited on a tilted OFHC copper wedge at 15 K, were recorded using krypton ion laser lines (476.2, 530.9, 568.2 nm) and a Spex Ramalog with DC amplification.¹⁰

RESULTS

Spectroscopic observations from infrared, Raman, and optical experiments will be presented.

Infrared

The optical quality of matrices containing zinc atoms was difficult to maintain owing to light scattering from unreacted metal. In the first zinc experiment, the sample was deposited on a 15 K substrate; in subsequent experiments, improved sample transmission was obtained using a 20 K window. Infrared spectra of zinc-ozone reaction products in nitrogen matrices are shown in Fig. 1 for (a) ${}^{16}O_3$, (b) ${}^{16,18}O_3$, and (c) ${}^{18}O_3$ and the product absorptions are listed in Table I.

Very strong bands were observed at 396 cm⁻¹ with ${}^{16}O_3$ and 383 cm⁻¹ with ${}^{18}O_3$. A broad, less intense band,

TABLE I. Absorptions (cm⁻¹) and assignments of new bands observed in nitrogen matrix reactions of zinc and ozone.

$Zn + {}^{16}O_3$	Zn + ^{16, 18} O ₃	$Zn + {}^{18}O_3$	Assignment
283.2	283, 269	268.8	ZnOZn
396	385 389 393	383	$(Zn^{+} \leftrightarrow O_{3}^{-})^{a}$
539.5	513.7 525.2 539.3	513.5	ZnO_2
697		661	(ZnO-O ₂ ?)
710.0	(b)	671.0	$(\mathrm{ZnO}_3)^{\mathbf{a}}$
741.3	742,729	728.7	68 ZnO–O ₂
744.6	745, 733	732.0	66 ZnO–O ₂
748.2	748, 736	735.5	64 ZnO $-O_2$
802		766	ZnO
805.8 809.2 810.9	811, 775	769.7 772.3 775.0	⁶⁸ ZnO ⁶⁶ ZnO ⁶⁴ ZnO
831	(b)	785	ZnO_3
843.4	(b)	797.5	ZnO3

^aDifferent (Zn⁺) (O_3) ion-pair arrangement than 843 cm⁻¹ absorber.

^bUnresolved intermediate absorptions.



FIG. 1. Infrared spectra of zinc-ozone reaction products condensed in solid nitrogen. (a) $N_2/{}^{16}O_3 = 130$, 45 mmol deposited at 15 K with low Zn concentration, (a') same sample following 30 min 220-1000 nm mercury arc photolysis; (b) $N_2/{}^{16}O_3 = 150$, 47 mmol deposited at 20 K with low Zn concentration, (b') same sample following 340-, 290-, and 220-1000 nm photolysis; (c) $N_2/{}^{16}O_3 = 200$, 65 mmol deposited at 20 K with increased Zn concentration, (c') same sample following 290-1000 and 290-1000 nm photolysis.

centered at 389 cm⁻¹ was observed with ^{16,18}O₃, with partially resolved structure at 385, 399, and 393 cm⁻¹. In the 15 K ¹⁶O₃ experiment, the band was photolysed completely with 220-1000 nm light; however, in the isotopic experiments, the product absorption was reduced but not destroyed by photolysis. A resolved triplet was observed in the scrambled experiment, at 513.7, 525.2, and 539.3 cm⁻¹, with the 1-2-1 relative intensities expected for a two equivalent oxygen atom species. Single bands at 513.5 and 539.5 cm⁻¹ were observed in the pure isotope experiments. The 539 cm⁻¹ band, and a small side band at 517 cm⁻¹, were completely destroyed by 220-1000 nm photolysis. In the scrambled isotope ex-

periment, the bands were successively decreased by photolysis with 340-, 290-, and 220-1000 nm radiation. The pure ${}^{18}O_3$ products decreased following both 290- and 220-1000 nm photolysis.

Carbon dioxide was observed at 663 cm⁻¹, and isotopic exchange with the ozone samples produced 653 and 658 cm⁻¹ bands due to $C^{18}O_2$ and $C^{16}O^{18}O$ in $^{18}O_3$ and $^{16,18}O_3$ experiments. Two prominent new absorptions appeared in this region, a band at 697 cm⁻¹, and a sharper feature at 710.0 cm⁻¹ with $^{16}O_3$, and corresponding bands at 661 cm⁻¹ as a shoulder on CO_2 , and at 671.0 cm⁻¹ with $^{18}O_3$. As shown in trace (*a'*) of Fig. 1, the 697 cm⁻¹ band was substantially

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decreased, and the 710.0 cm⁻¹ band was destroyed by 220–1000 nm photolysis. The mixed isotope experiment showed a weak 679 cm⁻¹ shoulder on the ¹⁸O¹⁸O¹⁶O band, and small, sharp features at 692.5 and 710 cm⁻¹. In addition, the 672, 689, and 704 cm⁻¹ ozone bands were roughly double the expected relative intensities, compared to the other three ozone features. The 710 cm⁻¹ and extra intense 672 cm⁻¹ ozone bands correspond to the sharp new features in the separate ¹⁶O₃ and ¹⁸O₃ isotope experiments. There were no absorptions in the ^{16,18}O₃ experiments for the 697 and 661 cm⁻¹ bands observed in the pure isotope spectra.

A new feature, observed only after photolysis, consisted of two triplets, each having the approximately 5-3-2 relative intensities expected for natural abundance zinc isotopes. The stronger triplet appeared at 748.2, 744.6, and 741.3 cm⁻¹ with ${}^{16}O_3$, and a weaker triplet, probably a site effect, came at 736.2, 732.6, and 729.1 cm⁻¹. This feature was destroyed by thermal cycling. Bands were observed at 735.5, 732.0, and 728.7 cm⁻¹ in the ${}^{18}O_3$ experiment following 220-1000 nm photolysis, with the site feature at 720.4, 716.3, and 712.6 cm^{-1} . Using ^{16,18}O₃ the triplets grew more intense following exposure to 340-, 290-, and 220-1000 nm radiation. The bands appeared at 748, 745, 742 and 736, 733, 729 cm⁻¹, with the lower triplet slightly broadened and more intense, probably due to superposition of the site splitting of the upper band.

The next significant feature was a small broad band at about 802 cm⁻¹ with ${}^{16}O_3$ that was replaced following 290-1000 nm photolysis by a sharp, zinc isotope split triplet at 810.9, 809.2, and 805.8 cm⁻¹, superimposed on a slightly less intense triplet about 1.5 cm⁻¹ higher, which can be seen more clearly from expanded scale spectra. This multiplet grew further following 220-1000 nm photolysis. A corresponding feature was observed with ¹⁸O₃ at about 766 cm⁻¹, which was reduced by photolysis, while the triplet grew in at 775.0, 772.3, and 769.7 cm⁻¹, with the same 1.5 cm⁻¹ higher site splitting. These bands were obscured somewhat in the mixed isotope experiment by the scrambled ozonide features, but the principal components are readily observed at 775 and 811 cm⁻¹, as denoted by arrows in the figure. Significantly, no intermediate features (not attributable to ozonide) were observed in the mixed isotope experiment, indicating a single oxygen species is produced upon photolysis.

The next feature consisted of several bands of varying widths and intensities. In the low Zn concentration ${}^{16}O_3$ experiment, shown in Fig. 1(a), a broad band was observed at 831 cm⁻¹, and a stronger sharp one at 843.4 cm⁻¹ with shoulders at 823, 837, and 849 cm⁻¹. Photolysis with 220–1000 nm radiation destroyed the 837 cm⁻¹ shoulder, while the 831 cm⁻¹ band grew considerably and the 843.4 cm⁻¹ band was reduced by 40%. Similar features were observed in the ${}^{18}O_3$ experiment, with the principal bands appearing at 785 and 797.5 cm⁻¹. Only a broad, slightly structured band between 794 and 840 cm⁻¹ was observed with ${}^{16,18}O_3$, with some growth following each photolysis.

A second $N_2/{\rm ^{16}O_3}$ experiment was conducted with the 20 K substrate and a relatively high Zn concentration.

TABLE II. Absorptions (cm^{-1}) and assignments of new bands observed in nitrogen matrix reactions of cadmium and ozone.

$Cd + {}^{16}O_3$	$Cd + {}^{16,18}O_3$	$Cd + {}^{18}O_3$	Assignment
346	340	335	$(Cd^+ \leftrightarrow O_3^-)^a$
492		474	?
574.3	548.4 555.5 570.0 574.0	548.2	CdOO
655 659	(b)	625 629	(CdO-O ₂)
712	(c)	672	(CdO ₃) ^a
719.0	719,684	683.3	CdO
817.3	(c)	772.2	CdO_3
826.1		780.0	CdO_3
1 129	1 066 1 096 1 129	1066 '	CdOO

^aDifferent (Cd⁺) (O₃⁻) ion-pair arrangement than 826 cm⁻¹ absorber.

^bNo intermediate component observed.

^cUnresolved intermediate absorptions.

The spectrum was similar to Fig. 1(a) except the major product bands were virtually completely absorbing and a sharp, new product feature was observed at 283.2 cm⁻¹ (A = 0.24). Photolysis caused the same increases and decreases in absorption bands shown in the figure, but less markedly due to poor ultraviolet transmission of this sample. An oxygen-18 counterpart of the lowest wave number band was observed at 268.8 cm⁻¹ in the ¹⁸O₃ study.

The spectra of cadmium plus ozone in nitrogen samples are shown in Fig. 2, and all product absorptions are listed in Table II. Features not shown include weak bands at 346.5 cm⁻¹ with ¹⁶O₃ and at 335.5 cm⁻¹ with ¹⁸O₃. The mixed ozone study gave a broad intermediate band at 340 cm⁻¹. These bands were not affected by photolysis of thermal cycling. Two prominent bands are shown at 574.3 cm⁻¹ with ¹⁶O₃ and at 548.2 cm⁻¹ with ¹⁸O₃. The ^{16,18}O₃ counterpart appeared as two asymmetric doublets at 574.0, 570.0 and 555.5, 548.4 cm⁻¹. These bands increased following 220–1000 nm photolysis, as shown in the figure, and also following a thermal cycle.

The next section of the spectrum is dominated by CO_2 and O_3 bending vibrations; however, new features were observed as well. A pair of broad, poorly resolved doublets appeared at 659.3, 655.3 cm⁻¹ with ${}^{16}O_3$ and at 629.0, 624.5 cm⁻¹ with ${}^{18}O_3$. Photolysis slightly reduced these bands, and thermal cycling favored one component of each doublet, indicating that the splitting is probably due to matrix sites. In the mixed isotope experiment, the lower ${}^{18}O_3$ doublet was clearly observed, but the 659 cm⁻¹ component was obscured by the superimposed isotopic CO_2 bands at 653 and 658 cm⁻¹. However, the relative intensity of the CO_2 bands indicates that the ${}^{16}O_3$ feature was present as well, but no inter-



FIG. 2. Infrared spectra of cadmium-ozone reaction products condensed in solid nitrogen. (a) $N_2/{}^{16}O_3 = 260$, 56 mmol deposited; partial scans following 30 min 340-600 nm plus 30 min 220-1000 nm mercury arc photolysis; (b) $N_2/^{16,18}O_3 = 200, 66 \text{ mmol de-}$ posited; partial scans following 30 min 220-1000 nm mercury are photolysis; (c) $N_2/^{18}O_3 = 270$, 53 mmol deposited; partial scans following 290-1000 and 220-1000 nm photolysis.

mediate component was observed in the ${}^{16,18}O_3$ spectra. A product band at 712 cm⁻¹ was only slightly reduced by photolysis, but grew and broadened on warming. The only product band with ${}^{18}O_3$ before photolysis is a slightly broad feature at 672 cm⁻¹.

Two small bands were observed to grow in following photolysis as indicated with arrows in Fig. 2. With $^{16}O_3$, the band appeared at 719.0 cm⁻¹ following 340-480 nm photolysis, and grew further following 220-1000 nm exposure. A thermal cycle reduced, but did not destroy, the band. With $^{16}O_3$, the band shifted to 683.3 cm⁻¹, growing in after 290-1000 nm photolysis, and was not further affected by 220-1000 nm photolysis.

The mixed isotope spectra exhibited the six isotopic ozone bands at 665, 671, 681, 689, 697, and 705 cm⁻¹, with the appropriate relative intensities.¹¹ Shoulders on ozone bands were observed at 675, 699, and 709 cm⁻¹. Photolysis with 220–1000 nm radiation had little effect on these bands; however, a weak band grew in at 719 cm⁻¹, and a shoulder appeared at 684 cm⁻¹ on the 681 cm⁻¹ ozone band, corresponding to the bands produced by photolysis in the pure isotope experiments. No intermediate component was observed to grow in following photolysis in the ^{16, 18}O₃ experiment.

The next feature in each of these spectra was a strong, split band, having the same asymmetric structure in

TABLE III. Absorptions (cm^{-1}) and assignments of new bands observed in argon matrix reactions of cadmium and ozone.

$Cd + {}^{16}O_3$	Cd + ¹⁶ , ¹⁸ O ₃	Cd + ¹⁸ O ₃	Assignment
310	300 303 307	299	CdO _x ?
359	352	348	$(Cd^{+} \leftrightarrow O_{3}^{-})^{a}$
52 9	· (b)	504	?
559	(b)	533	?
576	551 575	549	CdOO
708 720	674 708 681 719	673 680	(CdO ₃) ^a (CdO ₃) ^a
817.0		771.5	CdO_3
822.5	(c)	776.5	CdO ₃
1 124	1 061 1 092, 1 093 1 124	1 061	CdOO

^aDifferent (Cd^{*}) (O₃^{*}) ion-pair arrangement than 822 cm⁻¹ absorber.

^bNo intermediate counterpart observed. ^cIntermediate absorptions.



FIG. 3. Infrared spectra of argon matrix reactions of zinc or cadmium metal and ozone. (a) $Ar/{}^{16}O_3 = 200 + Zn$, 54.0 mmol deposited; (b) $Ar/{}^{16}O_3 = 200 + Cd$, 67 mmol deposited; (c) $Ar/{}^{16}O_3 = 220 + Cd$, 60 mmol deposited; (d) $Ar/{}^{18}O_3 = 200 + Cd$, 66 mmol deposited.

both pure isotope experiments, with peaks at 817.3 and 826.1 cm⁻¹ with ${}^{16}O_3$, and 772.2 and 780.0 cm⁻¹ with ${}^{18}O_3$. The band in the scrambled experiment was broad, with structure at 772, 781, 791, 787, 808, 812, and 817 cm⁻¹, and small shoulder peaks on either side at 765 and 822 cm⁻¹. Photolysis and thermal cycling had little effect on these very strong absorptions.

The ozone stretching region was straightforward in these spectra, with ozone vibrations easily assigned.¹¹ Sharp weak bands at 1129 and 1066 cm⁻¹ appeared in the ${}^{16}O_3$ and ${}^{18}O_3$ experiments, the latter being too intense to be due to ozone alone. A weak 1129 cm⁻¹ band was observed in the ${}^{16},{}^{18}O_3$ experiment as well.

Argon matrix results are shown in Fig. 3, and bands produced in cadmium experiments are listed in Table III. One experiment was done with zinc and ozone using an argon matrix. A triplet was observed at 427, 424, and 420.5 cm⁻¹ with zinc isotopic relative intensities (not shown) and weak bands were observed at 592, 567, and 520 cm⁻¹. These bands were unaffected by 220-2000 nm radiation. A new band at 748 cm⁻¹ was only slightly reduced by photolysis. A strong, broad band was observed at 830 cm⁻¹, with smaller side bands at 813 and 844 cm⁻¹ which were generally unaffected by photolysis. In addition, a broad shoulder on this system was observed at 870 cm^{-1} .

The experiments with cadmium and ozone in argon gave product bands with comparable yields to their nitrogen matrix counterparts. In the region below 500 cm⁻¹, the major feature at 359 cm⁻¹ with ¹⁶O₃ was slightly increased by 220-1000 nm photolysis and decreased, but not destroyed, by a thermal cycle. A corresponding feature in the ¹⁸O₃ spectrum appeared at 348 cm⁻¹. A slightly broader band appeared in the ^{16,18}O₃ spectrum, centered at about 352 cm⁻¹.

Three other weak bands in the ${}^{16}O_3$ experiment are shown in Fig. 3 at 576, 559, and 529 cm⁻¹. With ${}^{16}O_3$ these bands shifted to 549, 533, and 540 cm⁻¹. In the ${}^{16}O_3$ experiment, a sharp new feature observed at 720 cm⁻¹ was unaffected by photolysis. In the ${}^{16}O_3$ experiment, additional new bands appeared at 673 and 680 cm⁻¹. The ${}^{16,18}O_3$ spectrum is congested in this region, but new bands can be seen at 668, 674, 681, 708, and 719 cm⁻¹.

A strong band was observed using ${}^{16}O_3$ with peaks at 817 and 822 cm⁻¹. A similar feature in the ${}^{18}O_3$ spectrum



FIG. 4. Raman spectra of argon matrix reactions of zinc and cadmium atoms with ozone using krypton ion laser excitation. Scan speed: $50 \text{ cm}^{-1} \text{ min}^{-1}$. Range: $0.1 \times 10^{-9} \text{ A}$. (a) Cd, $\text{Ar}/^{16}\text{O}_3 = 110$, 150 mW of 530.9 nm excitation, (b) Zn, $\text{Ar}/^{16}\text{O}_3 = 120$, 85 mW of 476.2 nm excitation.

falls at 771 and 776 cm⁻¹, with numerous sharp side bands. The $^{16,18}O_3$ spectrum shows a strong, broad, structured band encompassing both of the pure isotope bands, and revealing numerous intermediate features.

The ozone parent bands were intense in all three cadmium experiments in argon, and exhibited splittings characteristic of an argon matrix.¹¹ Other significant absorptions include a sharp band at 1124 cm⁻¹ in the ¹⁶O₃ experiment that was successively reduced by 340- and 220-1000 nm photolysis, and finally destroyed by a thermal cycle. A corresponding feature in the ¹⁸O₃ experiment appeared at 1061 cm⁻¹, also reduced by photolysis and by warming. In the ^{16,18}O₃ experiment, bands at 1062 and 1090 cm⁻¹ are attributable to the symmetric stretches of ¹⁸O¹⁸O¹⁶O and ¹⁶O¹⁶O¹⁸O, respectively,¹¹ but small sharp bands at 1061 and 1124 cm⁻¹ correspond to the sharp bands observed in the pure isotope experiments. In addition, a small, barely resolved doublet at 1092, 1093 cm⁻¹ corresponds to the intermediate mixed isotope counterpart.

Raman

Several Raman experiments were done in which ozone was deposited in argon with zinc or cadmium, and examined with the 476.2, 530.9, and 568.2 nm lines of a krypton ion laser. The cadmium samples could not be examined with the blue line, due to a strong green fluorescence from the metal dimer.¹² Figure 4(a) shows the Raman spectrum of a cadmium and ozone sample with a large product feature shifted 651 cm⁻¹ below the 530.9 nm laser line. Other prominent features are a broad band at 1014 cm⁻¹ and a moderately strong band at 1289 cm⁻¹, an overtone of the 651 cm⁻¹ band. Another scan of the same sample with 568.2 nm excitation again showed the strong 651 cm⁻¹ line, and a moderate 1286 cm⁻¹ overtone.

The zinc and ozone sample, shown in Fig. 4(b) using 476.2 nm excitation, exhibited a strong band at 769 cm⁻¹, a very strong feature at 1010 cm⁻¹, unreacted ozone¹¹ at about 1100 cm⁻¹, and oxygen at about 1555 cm⁻¹. A weak band at about 1540 cm⁻¹ is probably an overtone of the 769 cm⁻¹ band, while the 1010 cm⁻¹ band has overtones at about 2005 and 3000 cm⁻¹. The same bands were observed with 530.9 nm excitation, though the 1010 cm⁻¹ band is relatively less intense with the green laser. Other experiments were done with slightly varied ozone and metal concentrations, but no new features were observed, while those mentioned appeared with varying relative intensities.

Visible absorption

The optical absorption spectra for zinc and cadmiumozone samples are shown in Fig. 5. After 1 h of codeposition of Zn atoms from a 230-250 °C source with an $Ar/O_3 = 100/1$ sample, the spectrum of Fig. 5(a) was recorded; the vibronic bands with spacings ranging from 900 to 790 cm⁻¹ are listed in Table IV. In the corre-

TABLE IV. Vibronic band positions (cm^{-1}) and spacings observed for zinc and cadmium reactions with ozone in argon.

$v_1' = 0$	Zn	+ 16O ₃		Zn	+ 18O3		Cd	•0 3	
$v'_1 = 0$	18	310		18	320		18	532	
			900			860			904
1	19	210		19	180		19	440	
2	90	105	893	20	0.1.0	860	20	994	894
4	20	105	882	20	040	850	20	334	871
3	20	987	002	20	890	000	21	205	011
			841	_		830			855
4	21	828		21	720		22	060	
			835			790			850
5	22	663		22	510		22	910	
0	0.0	-00	845	00	800	790			824
0	23	508	896	23	300	767	23	734	007
7	24	334	020	24	067	101	24	571	007
			79 0		•••	760		0.1	816
8	25	134		24	827		25	387	
			798			758			799
9	25	932	- • -	25	585		26	186	
10	90	7 99	790	96	995	740	50	050	793
10	26	122	819	20	325	770	26	979	704
11	27	534	012	27	104	115	27	773	(34
			808			763		110	798
12	28	342		27	867		28	571	
						737			
13				28	604				

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FIG. 5. Optical spectra of zinc and cadmium-ozone matrix reaction products using matrix/ozone (200/1) samples. (a) $Ar/^{16}O_3$, Zn from 230-250 °C source for 1 h, (b) $Ar/^{18}O_3$, Zn from 200-220 °C source for 4 h, (c) $Ar/^{16}O_3$, Cd from 190-200 °C source for 4 h, (d) N_2/O_3 , Zn from 220-240 °C source for 4 h.

sponding $Ar/^{18}O_3 = 200/1$ experiment, Zn atoms from a 200-220 °C source were deposited for 4 h and the spectrum, shown in Fig. 5(b), exhibit a similar structured absorption; however, the vibronic spacings were decreased ranging from 860 to 737 cm⁻¹ and the scattering background was reduced. The first vibronic bands in the ¹⁸O₃ and ¹⁸O₃ spectra agree within ± 10 cm⁻¹, the measurement uncertainty, but the 8+0 transitions show an appreciable oxygen isotopic shift, 307 ± 20 cm⁻¹, as illustrated by dashed lines in the figure. Zinc atoms were also codeposited with a N₂/O₃ = 170/1 sample for 4 h which produced a faint yellow sample having the absorption spectrum in Fig. 5(d). The vibronic bands were *blue shifted* 3 nm from their argon matrix positions.

The sample was subjected to 220-1000 nm photolysis for 30 m; the yellow color paled, the vibronic bands were halved, the background scatter was reduced and no new absorptions were observed out to 700 nm. Photolysis and sample deposition for an additional 2 h also produced no changes in the spectrum.

The absorption spectrum for a cadmium experiment is contrasted in Fig. 5(c) and the vibronic bands are listed in Table IV. The cadmium product spectrum is similar to the zinc product spectrum except for a $220-260 \text{ cm}^{-1}$ blue shift in the vibronic peaks.

DISCUSSION

The several different zinc and cadmium oxygen-containing products will be identified and compared to other similar metal species.

Metal ozonides

In previous matrix studies of metal-ozone systems, the 800-850 cm⁻¹ region contained at least one strong sharp band that has been assigned to a $M^*O_3^*$ species.¹⁻⁵ In the present study, strong bands at 843.4 and 826.1 cm^{-1} are assigned to the $Zn^+O_3^-$ and $Cd^+O_3^-$ ion-pairs in solid nitrogen. Oxygen-18 counterparts of these bands were observed at 797.5 and 780.0 cm^{-1} , respectively. The assignment of these bands in previous studies to the ν_3 antisymmetric O₃ vibration was based on the greater intensity, relative to other ozonide features, analogous to the neutral ozone molecule. The assignment of these bands to a pure oxygen mode that does not involve the metal atom is supported here, as in previous work, by the 16/18 isotopic frequency ratios, 843.4/797.5= 1.0576 and 826.1/780.0 = 1.0591, in good agreement with a pure oxygen vibration which exhibits a 1.0608 isotopic ratio.

In both zinc and cadmium experiments, other strong bands were observed in the ozonide region, principally at about 831 and 785 cm⁻¹ with zinc plus ${}^{16}O_3$ and ${}^{18}O_3$, respectively, and at 817 and 772 cm⁻¹ with cadmium. Their isotopic ratios, 1.0586 and 1.0584, again indicate an oxygen vibration, and these bands are also assigned to an ozonide. In the zinc experiments, this broader feature grows following photolysis and temperature cycling, indicating perhaps a more stable ozonide geometry, differing in the position of the metal cation, rather than by a change in the shape of the ozonide anion. In argon matrix experiments the same two main ozonide bands were observed, at 831, 843 cm⁻¹ with zinc and $^{16}O_3$, at 817, 822.5 cm⁻¹ with cadmium and $^{16}O_3$, and at 771.5, 776.5 cm⁻¹ with cadmium and ¹⁸O₃, exhibiting little, if any, shift due to the different matrix.

The features in the ozonide region in both zinc and cadmium experiments are broader, and show more site effects than in previous metal-ozone studies. It is not surprising, then, that the bands in the mixed oxygen isotope experiments do not show the clearly resolved sextet, characteristic of a two equivalent, three oxygen species, as was observed in alkali metal and alkaline earth metal studies. $^{1-5}$ It is clear from the spectra, however, that the broad, slightly structured feature encompassing

the region of the pure isotope ozonide bands is the mixed isotope ozonide counterpart, including the unresolved isotopic multiplets of the two ozonide bands.

In the zinc and ozone experiments in nitrogen matrices two intense bands were observed at 710.0 and 697 cm⁻¹ with ${}^{16}O_3$. Oxygen-18 counterparts were observed at 671.0 cm^{-1} and as a shoulder on the CO₂ band at about 661 cm⁻¹. The oxygen isotope ratios of 710.0/671.0=1.0581 and 697/661 = 1.504 indicate that a largely oxygen vibration is responsible for these features. These bands are too intense relative to the higher frequency ozonide bands to be a different mode of the same species based on the relative intensity of the ν_2 and ν_3 parent ozone bands¹¹ and their dramatically different photolysis behavior. Although the $710-671 \text{ cm}^{-1}$ region contains mixed isotopic ozone precursor as well as product features, definite isotopic product assignments cannot be made. The observation of some mixed isotopic bands supports assignment of the 710 and 671 cm⁻¹ bands to a $Zn^+O_3^-$ species of a different structural arrangement. The 697 cm⁻¹ feature may also be another ozonide which could be related to the 659, 655 cm^{-1} absorption in cadmium studies.

Experiments with cadmium and ozone in nitrogen revealed a single feature, at 712 and 672 cm⁻¹ with ¹⁶O₃ and ¹⁸O₃, respectively. Again, the mixed isotope features are difficult to separate from the parent ozone; however, a careful examination of the ozone bands indicates that some other features are present as well. These bands are thus also assigned to a small yield of an ozonide of different geometry from the 800 cm⁻¹ ozonide. Comparison of yields with the higher frequency ozonide in cadmium experiments indicates that the higher frequency species is the favored cadmium ozonide.

The experiments with zinc or cadmium and ozone in argon matrices produced very intense ozonide bands near 800 cm⁻¹, but only weak bands in the 700 cm⁻¹ region. These weaker bands, 748 cm⁻¹ with Zn and 720 cm⁻¹ with Cd, are probably due to different $B^*O_3^-$ structural forms.

The assignment of infrared absorptions near 700 cm⁻¹ to Zn and Cd ozonides with a different cation-anion arrangement is supported by the observation of intense Raman bands at 651 cm⁻¹ with cadmium and 769 cm⁻¹ with zinc, in addition to the intense resonance Raman signal near 1010 cm⁻¹ due to the same type of ozonide observed in previous metal-ozone studies. ^{6,8} The observation of overtones for the new ozonide bands suggests that this $B^+O_3^-$ species also absorbs in the near ultraviolet, as does the normal O_3^- species, ^{7,6} which dominates the absorption spectra of the present matrix samples.

Absorption spectra for zinc and cadmium-ozone samples reveal the vibronic ozonide progression typical of the alkali metal $M^*O_3^-$ and alkaline earth metal $A^*O_3^$ species, which shows that +1 oxidation states of zinc and cadmium are prepared here. The vibronic spacings of the ozonide ion in $Zn^*O_3^-$ and $Cd^*O_3^-$ are comparable to the group IA and IIA species.^{7,8} The $Cd^*O_3^-$ vibronic origin is about 200 cm⁻¹ higher energy than the $Zn^*O_3^-$ origin, and both group II origins fall $300-700 \text{ cm}^{-1}$ to the blue of the alkali ozonides.

Another set of bands appeared in the nitrogen matrix zinc experiments, at 396 cm⁻¹ with pure ${}^{16}O_3$, at 383 cm⁻¹ with ¹⁸O₃, and as a broad band at 389 cm⁻¹, with slight structure peaking at about 385 and 393 cm⁻¹ in the ^{16,18}O, experiment. The fact that the obvious shoulders occur between the pure isotope positions and the center of the band in the mixed isotope experiment indicates contributions from several mixed isotope combinations, thus the species responsible for this band contains more than two oxygen atoms. These bands are therefore assigned to the $M^{\bullet} \leftrightarrow O_3^{-}$ interionic stretch of the oxonide. This assignment is supported by the pure oxygen isotopic ratios, 396/383 = 1.0339, in excellent agreement with the 1.0334 value calculated for a zinc atom vibrating against a mass equivalent to three oxygen atoms. The asymmetry to the low frequency side of the pure isotopic bands is indicative of unresolved zinc isotope splitting. It is of interest to determine which type of ozonide this band may be associated with, those near 800 cm⁻¹, or those near 700 cm⁻¹. The most significant clue to this question is the photolysis behavior, shown dramatically in the ${}^{16}O_3$ experiment, where the band is completely destroyed by 220-1000 nm photolysis. This is the behavior observed for the sharp ozonide band at 710 cm⁻¹, and in both the mixed isotope and $^{18}O_3$ experiments, these bands again exhibited parallel behavior on photolysis. A small zinc isotope split triplet in the argon matrix experiment at 427, 424, and 420.5 cm^{-1} might also be assigned to the interionic stretch for the ozonide observed at 748 cm⁻¹.

The cadmium experiments in nitrogen might reasonably be expected to exhibit an interionic ozonide feature as well, and weak bands at 346.5 cm^{-1} with $^{16}\text{O}_3$ and at $335.5\ {\rm cm^{-1}}\ {\rm with}\ {^{18}O_3}\ {\rm are}\ {\rm assigned}\ to\ this\ vibration.$ The mixed oxygen isotope experiment produced a broad band at 340 cm⁻¹, the relative intensity of which indicates isotopic dilution. The cadmium reactions in argon produced strong 800 cm⁻¹ ozonide bands, but only very weak features in the 700 cm⁻¹ region that were reduced on thermal cycling. A set of bands at 359 cm⁻¹ with ${}^{16}O_3$, at 348 cm⁻¹ with ${}^{18}O_3$, and a broad, less intense band at 352 cm⁻¹ with $^{16,18}O_3$, are clearly reduced on thermal cycling as well. In the ${}^{16}O_3$ experiment, the 720 cm⁻¹ ozonide band is more intense than its counterparts in the other two isotope experiments. Likewise, the yield of the 359 cm⁻¹ species is noticeably larger than its counterparts in the isotope experiments. These observations lead to the assignment of this mid-300 $\rm cm^{-1}$ set of bands to the interionic metal-ozonide stretch of the 700 cm⁻¹ ozonide in argon.

Reactions between magnesium and ozone in argon produced ozonide in the 800 cm⁻¹ region, and in addition, a set of bands in the low 700 cm⁻¹ region exhibited isotopic splittings appropriate for a single metal vibrating primarily against a single oxygen atom with a small dependence on two additional equivalent oxygen atoms.¹ This species was also characterized by magnesium and oxygen isotopic shifts showing more Mg and less O dependence than μ_{Mg} + μ_{O} . The sharp triplet absorption at 748.2, 744.6, and

741.3 cm⁻¹ produced by photolysis in Zn, ${}^{16}O_3$ experiments displays the same isotopic shift characteristics. The 5/3/2 relative intensities are due to ⁶⁴Zn, ⁶⁶Zn, and ⁶⁸Zn isotopes in natural abundance, which demonstrates the participation of a single zinc atom, and the 3.4 ± 0.2 cm⁻¹ zinc isotopic shifts are larger than the 2.3 cm⁻¹ shift for a harmonic diatomic ZnO molecule. Likewise the ${}^{18}O_3$ counterpart triplet at 735.5, 732.2, and 729.0 cm⁻¹ displays large Zn splittings and a 12.7 cm⁻¹ oxygen isotopic shift, which is smaller than the 34.1 cm^{-1} shift expected for a pure ZnO vibration. The ^{16, 18}O₃ experiment gave a doublet of zinc triplets indicating a primary dependence on a single metal atom; however, the zinc and oxygen isotopic shifts rule out ZnO itself. The 748 cm⁻¹ triplet, which appears on photolysis, is probably due to a photoisomer of ZnO₃ in a structure where the Zn is bound to a single oxygen, like

$$\mathbb{Z}n - 0 < 0^{0}$$
.

A pair of doublets at 655 and 659 cm⁻¹ with ${}^{16}O_3$ and at 625 and 629 cm⁻¹ with ${}^{18}O_3$ were observed in cadmium experiments in nitrogen. Both were observed in the 16 , ${}^{18}O_3$ experiment as well, with no intermediate counterpart. These bands were slightly reduced by photolysis. Similar behavior was found for the 697-661 cm⁻¹ bands in zinc studies. These bands may also be due to a

ozonide species.

The principal ozonide band with sodium, calcium, strontium, and barium cations was observed at 804 cm⁻¹. These bands were intense and sharp and occurred as well-resolved sextets in ^{16, 18}O₃ experiments. ^{4, 5} It is suggested that the 800 cm⁻¹ absorbing $M^+O_3^-$ species have a pyramidal ion-pair structure with M^{+} above the O_{3}^{-} plane, as found for Na⁺O₃⁻ in ESR studies.¹³ In contrast, zinc and cadmium produced intense but broader bands at slightly higher frequencies and new bands in the 700 cm⁻ region identified as structural isomeric $B^+O_3^-$ species. It is suggested that Zn^{*}and Cd^{*} ions must be closer to O_3^- to support charge transfer from the higher ionization energy metals, which gives more metal affect on the ozonide vibrations and on the several ion-pair geometries. The 700 cm^{-1} absorbing ozonides may have a coplanar ion-pair structure.

Metal oxides

In zinc-ozone experiments, weak bands at 802 cm⁻¹ with ${}^{16}O_3$ and 766 cm⁻¹ with ${}^{18}O_3$ were reduced on photolysis which produced sharp triplets at 810.9, 809.2, and 805.8 cm⁻¹ and at 775.0 772.3, and 769.7 cm⁻¹. Each exhibited a site splitting about 1.5 cm⁻¹ higher than the main bands; both the bands and their sites showed the 5-3-2 relative intensities expected for the vibration of a single Zn atom with three principle zinc isotopes in natural abundance. In the mixed isotope experiments, both isotope features were observed, as noted with arrows in the figure, superimposed on a broad, unresolved mixed isotopic ozonide feature. No intermediate

TABLE V. Observed and calculated frequencies (cm^{-1}) for six isotopic combinations of the zinc oxide molecule.

Average force constant = 4.967 mdyn/ \check{A}					
Isotope	Observed	Calculated	Difference ^a		
64-16	810.9	811.3	0.4		
66-16	808.2	808.8	0.6		
68-16	805.8	806.5	0.7		
64-18	775.0	774.3	-0.7		
66 - 18	772.3	771.7	-0.6		
68-18	769.7	769.3	-0.4		

^aDifference = calculated - observed.

feature was observed, indicating the vibration of a single oxygen atom.

The isotope shifts for both zinc and oxygen confirm the assignment of these bands to the ZnO molecule. An effective check of the isotope shifts is to compare the observed frequencies to those calculated using an average harmonic force constant; the observed and calculated frequencies are tabulated in Table V. While the agreement between observed and calculated frequencies for the ZnO molecule is not as close as for the MgO molecule $(\pm 0.3 \text{ cm}^{-1})$, ¹ the larger average difference for ZnO $(\pm 0.6 \text{ cm}^{-1})$ can be part be due to difficulty in obtaining accurate positions of the crowded bands on a sloping background. The calculated frequencies are slightly low for all the heavy isotopic molecules (Zn¹⁸O), and slightly high for all the light isotopic species $(Zn^{16}O)$, which is due to the use of an average harmonic oscillator force constant, because of different anharmonicity in the vibration of each isotopic molecule.

The observation of a weak 802 cm⁻¹ band after sample deposition just below the photolytically generated ZnO absorption at 810 cm⁻¹ is an indication that some ZnO is formed from Zn-O₃ reactions during sample condensation. The growth of ZnO on photolysis may be due to a simple Zn reaction with O atoms from O₃, since N₂O also appears on photolysis, or to the decomposition of ZnO₃ to ZnO and O₂. No new optical absorption was observed after photolysis that could be assigned to ZnO. This is not surprising, however, as the red CaO electronic transition was also too weak to be observed in similar calcium-ozone samples.⁸

Two features in cadmium-ozone reactions in nitrogen can be assigned to the CdO molecule. New bands were observed at 719.0 cm⁻¹ with ¹⁶O₃ and at 683.3 cm⁻¹ with ¹⁸O₃ only following photolysis. Both were weakly seen in the mixed isotope experiment, where no intermediate mixed isotope counterpart was observed. The frequency ratio, 719.0/683.3 = 1.0522 is in good agreement with that predicted by a harmonic calculation, 1.0526. The observed value is slightly below the calculated one, due to anharmonicity. The failure to resolve cadmium isotopes is not unreasonable, considering the number of abundant isotopes, and the small relative mass difference between them. The zinc and cadmium oxide assignments can be further justified by a comparison of oxide and fluoride frequencies for the metals and their Group IIA counterparts, calcium and strontium. A correspondence should exist between the CaO and CaF frequencies, and those of ZnO and ZnF. Thus it should be possible to predict an appproximate ZnO frequency from the vibrational data for these diatomic molecules.¹⁴ Analogous data for

$$\omega_{ZnO} \approx \omega_{ZnF} \times \omega_{CaO} / \omega_{CaF}$$

 $\omega_{ZnO} \approx 625 \text{ cm}^{-1} \times (713 \text{ cm}^{-1} / 587 \text{ cm}^{-1}) = 781 \text{ cm}^{-1}$.

SrO, SrF, and CdF predict 707 cm^{-1} for CdO. These estimated gas-phase fundamentals for ZnO and CdO are in very good agreement with the nitrogen matrix values.

No gas phase vibrational data are available for comparison of the matrix shifts of ZnO and CdO to MgO, which exhibited a 53 cm^{-1} blue shift, ¹ and CaO and SrO which exhibited 15 and 25 cm⁻¹ red shifts.³ In a mass spectroscopic study of the group IIA oxides, it was suggested that the failure to observe ZnO and CdO is due to their low dissociation energies, ¹⁵ although a recent observation of CdO by Knudsen effusion mass spectrometry inferred otherwise.¹⁶ The nitrogen matrix force constant for ZnO, 4.967 mdyn/Å. is higher than the 3.364 mdyn/ Å value for CaO,² which suggests a substantial dissociation energy for ZnO, although not necessarily higher than the 93 ± 5 kcal/mole value reported for CaO.¹⁵ The difficulty in observing ZnO is perhaps due to ease of chemical reduction rather than physical instability. Gas phase studies with the $Zn-O_3$ reaction used here should be able to detect the ZnO molecule.

Metal dioxides

In both the zinc and cadmium experiments, a set of bands was observed whose oxygen isotopic splittings clearly indicated a two oxygen species. However, the symmetric metal-superoxide ion pair from previous studies^{1-4, 17} was not observed here.

With zinc and $^{16}O_3,$ an intense, sharp band was observed at 539.5 cm $^{-1}.~$ The $^{18}O_3$ counterpart fell at 513.5 cm $^{-1},$ and the mixed isotope experiment contained a clearly resolved 1-2-1 relative intensity triplet at 513.7, 525.2, and 539.3 cm⁻¹. The isotopic ratio, 539.5/513.5 ==1.0507, is close to that for a Zn-O vibration, 1.0478, but is not an exact fit, and the intermediate band clearly indicates two equivalent oxygen atoms. The 539 cm⁻¹ band could be due to a rhombus-shaped dimer $(ZnO)_2$, although the strength of this band in low Zn concentration experiments argues for a single zinc atom species. The metal and oxygen isotopic dependence for the B_{2u} vibration of this species is the same as that for the diatomic.¹⁸ However, $(ZnO)_2$ would have another infrared active B_{3n} mode with observable intensity, $100 \text{ to } 200 \text{ cm}^{-1}$ below this band, and no such feature was found. The failure to observe the second mode of this species rules out a possible $(ZnO)_2$ assignment for the 539 cm⁻¹ feature.

Another viable assignment for these features is to the symmetric metal superoxide ion pair, $M^*(O_2)^*$. Assuming this assignment, the O-M-O angle can be calculated from the oxygen isotopic frequencies using the G-matrix

element for the antisymmetric stretch, $G_{33} = \mu_M + \mu_O$ - $\mu_M \cos \alpha$, ¹⁷ which gives an O-M-O angle of 79°. This angle is larger than those calculated for other metal superoxide species, ^{1, 17} and in fact, an angle this large requires close approach of the metal cation to the $O_2^$ ion. Assuming a superoxide anion bond length of 1.33 A, determined from x-ray diffraction of the NaO₂ crystal, ¹⁹ and the 79° angle, the M-O distance is calculated to be 1.05 A. While the large zinc ionization energy may necessitate a close approach for charge transfer to take place, reasonable radii of the zinc ion and the large superoxide anion indicate that this M-O distance is certainly too short. The assignment of these bands to the Zn^{*}(O₂)⁻ species is unlikely.

It is possible to get around the geometry restrictions calculated above, however, if the oxygen-oxygen bond is assumed to be broken, and a covalent, bent O-Zn-O molecule is postulated. This molecule could easily have the calculated bond angle, once the restriction of the oxygen distance is removed, and show the observed oxygen isotope intensities and splittings. This assignment is suggested for the 513, 525, 539 cm⁻¹ triplet.

The cadmium experiments did not produce a counterpart of the zinc dioxide triplet, but a moderately intense band at 574.3 cm⁻¹ with ${}^{16}O_3$ shifted to 548.2 cm⁻¹ with $^{18}O_3$, and the mixed isotope experiment revealed two doublets at 548.4, 555.5 and 570.0, 547.0 cm^{-1} . The lower frequency component of each doublet was slightly favored in each case. These bands all grew on photolysis, but were slightly decreased by thermal cycling in the pure ${}^{16}O_3$ and ${}^{18}O_3$ experiments and destroyed in the $^{16, 18}O_3$ experiment. The quartet observed in the mixed isotope experiment is consistent with assignment to a species with two inequivalent oxygens, CdOO. The asymmetry in the intensities is a slightly exaggerated demonstration of the 54% 18 O, 46% 16 O content of the scrambled sample. Bands in the cadmium and ozone experiments in argon matrices at 576.0 cm⁻¹ with ¹⁶O₃ and 549.5 cm⁻¹ with ${}^{18}O_3$ are probably due to the same species. Again, photolysis growth was observed. In the mixed isotope experiment, weak broad bands were observed at about 551 and 575 cm⁻¹, which are the unresolved mixed isotope doublets.

The pattern of the four bands observed in the mixed isotope experiment, two clearly separated doublets, is indicative of a vibration involving principally one oxygen atom, with a lesser influence from the second oxygen. In a CdOO molecule, this is the expected behavior for the vibration dominated by motion between cadmium and the adjacent oxygen. Another mode would then be expected, dominated by motion between the two oxygens, which might therefore fall in the oxygen stretching region, above 1100 cm⁻¹. Indeed, in the argon experiments, a sharp band was observed at 1124 cm⁻¹ with ${}^{16}O_3$ and at 1061 cm^{-1} with ${}^{18}O_3$, having an isotopic ratio of 1124/1061 = 1.0594, close to that of a harmonic pure oxygen mode. The pure ${}^{18}O_3$ feature includes a contribution from ν_1 of one of the scrambled ozones, but is is too intense relative to its ν_3 counterpart to be due to ozone only. In the mixed isotope experiment, the $^{18}O_3$ band has a sharp shoulder corresponding to v_1 of the mixed isotope ozone, while the mixed isotope cadmium feature appears as a broadened band, including the other mixed ozone ν_1 band, at 1092 cm⁻¹. The intensity and width of this mixed isotope feature suggests an unresolved doublet, rather than a single band with twice the intensity of the pure isotope bands. These observations are consistent with assignment to the oxygen stretch of the CdOO species. The singlet, doublet, singlet makeup of this upper quartet is expected from a lightly perturbed oxygen-oxygen stretch, the counterpart of the slightly perturbed cadmium-oxygen stretch observed at lower frequency. Similar splittings for the two stretches of an asymmetric molecule were observed for ClOO.²⁰

The nitrogen matrix counterparts of the oxygen stretching bands mentioned above are not easily differentiated from the ozone bands. They appear slightly broader, and coincide more closely with the ozone features. A weak band at about 1129 cm⁻¹ is clearly observed with ¹⁶O₃, and a band at 1066 cm⁻¹ with ¹⁸O₃ is too intense to be attributed to ν_1 of the mixed ozone alone. In the mixed isotope experiment, the 1129 cm⁻¹ band is weak, and the other two bands are obscured by the strong mixed ozone bands. Thus, there is some evidence for the oxygen stretch of CdOO in nitrogen as well.

The observation of almost no matrix shift for the CdOO species between argon and nitrogen is an indication that this molecule has little ionic character. This species may be similar to the zinc species, then, in terms of being covalently bonded, rather than being a metal cation-superoxide anion pair. An experiment with cadmium and oxygen did not produce this feature. While the corresponding experiment with zinc and oxygen was not done, the failure to observe either the cadmium or the magnesium¹ two-oxygen species following reaction with molecular oxygen indicates that the higher ionization energy zinc atoms would probably be unreactive with oxygen as well.

The mechanism of formation of the two-oxygen species, which seems to require an ozone intermediate, is worthy of speculation. Both the zinc and cadmium species are formed prior to photolysis, presumably by mechanisms similar to those proposed for MgO_2 , Reactions (1) and $(2)^1$:

$$M + O_3 - MO_2 + O \tag{1}$$

$$MO_3 + M - MO_2 + MO.$$
 (2)

The first reaction requires dissociation of ozone (26 kcal/mole), 21 and it is reasonable for the metal bonds formed to account for this energy. The second mechanism is consistent with the formation of the MO molecule, but the observation of the dioxygen species in low concentration zinc experiments suggest that a single metal atom is involved. Finally, growth of the cadmium species on photolysis is reasonable, both from decomposition of ozonide, or by addition of an oxygen atom from ozone to the CdO molecule.

Possible dizinc monoxide

A sharp, new band was observed at 283.2 ± 0.3 cm⁻¹ in the high Zn concentration experiment with ${}^{16}O_3$. This feature increased twofold more relative to the 539 cm⁻¹ band in the higher Zn concentration experiment compared to the lower Zn concentration study. Accordingly, the absorber probably contains two Zn atoms. A sharp ¹⁸O₃ counterpart was observed at 268.8 ± 0.3 cm⁻¹, and weak 283 and 269 cm⁻¹ bands *without* intermediate components were observed in the ^{16, 18}O₃ experiment, which suggests a single O species. The 16/18 isotopic ratio for a linear Zn-O-Zn molecule is 1.05348, almost exactly the observed 1.05357 ratio, which supports a possible ZnOZn assignment.

CONCLUSIONS

Matrix reactions of zinc and cadmium atoms with ozone produced the $B^+O_3^-$ ion-pair with similar infrared, Raman, and optical spectra to the alkali and alkaline earth metal reaction products. In addition, infrared and Raman evidence was found for $B^+O_3^-$ species with a different ion-pair geometry. Mercury arc photolysis of these samples reduced ozonide absorptions and produced zinc isotopic triplets at 810 cm⁻¹ in solid nitrogen which exhibited the expected oxygen-18 shift for ZnO. A new 719 cm⁻¹ band showed the proper oxygen-18 shift for CdO in the cadmium-ozone experiments. This work provides the first spectroscopic observation of the ZnO and CdO molecules. Evidence is presented for dioxygen species with zinc and cadmium.

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