Reaction of Pulsed Laser Evaporated Magnesium Atoms with Oxygen. Infrared Spectra of Linear OMgO and MgOMgO in Solid Argon

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Pulsed laser evaporated magnesium atoms were codeposited with O_2 in excess argon on a 10 K substrate. The sharp dominant product band at 767.7 cm⁻¹ showed magnesium and oxygen isotopic splittings and shifts in excellent agreement with shifts predicted for linear OMgO. Sharp 971.7- and 591.7-cm⁻¹ bands exhibited isotopic shifts appropriate for the linear MgOMgO species. The pulsed laser evaporation process imparts sufficient kinetic energy to Mg atoms to provide the activation energy for insertion into the O_2 molecule.

Introduction

Pulsed laser evaporated B atoms have been reacted with O_2, and the linear O–B–O molecule is the major product.[1,2] In the case of Al, pulsed laser evaporation gave linear O–Al–O as a major product in addition to cyclic AlO_2.[3] Photolysis increased linear O–Al–O and decreased cyclic AlO_2, and annealing the sample to allow diffusion and reaction of cold Al atoms had the reverse effect. These observations led to the conclusion that the insertion of Al requires activation energy while the addition reaction does not.[3] Pulsed laser evaporation experiments were performed with Ga and In specifically to search for new linear O–Ga–O and O–In–O species not formed with thermally produced atoms,[4] and the linear species were major products with translationally hot atoms from pulsed laser evaporation.[5]

An atom with limited ground-state reactivity is magnesium. Several attempts in this laboratory gave no product for the co-condensation reaction of thermally generated Mg with O_2 in excess argon.[6] In excess nitrogen, however, weak bands appropriate to ozonide species were observed.[7] Gas-phase studies have found that the Mg + O_2 reaction is very slow[8-11] but that the rate is about 3 times faster in nitrogen carrier gas than in helium.[12] It appeared reasonable that thermally and/or electronically excited magnesium atoms might insert to form a linear O–Mg–O species. Very recent theoretical calculations have predicted a $^3\Sigma_g^-$ linear ground-state structure and a ν_3 fundamental at 796 cm⁻¹ for OMgO.[13] The present pulsed laser experiments with Mg and O_2 further characterize this linear OMgO species.

Experimental Section

The pulsed laser experiments and infrared spectroscopy were performed using instruments described earlier.[1-3] A disk of magnesium metal (Fisher, rod), ^{26}Mg (Oak Ridge National Lab, pieces, >95%), fused MgO piece (Johnson Matthey), or a pressed (10 tons) pellet of MgO (Baker, reagent) was used as the rotating target. Laser energies of 10–20 mJ/pulse at the sample focused by a quartz lens (10-cm focal length) made tracks in the target approximately 0.1 mm wide. Infrared spectra were recorded on a Nicolet 60SXR spectrometer at 0.5-cm⁻¹ resolution and ±0.1-cm⁻¹ accuracy. Selected samples were photolyzed by the full light of a 175-W mercury arc and annealed, and more spectra were recorded.

Results

Investigations of pulsed laser evaporated Mg atoms codeposited with oxygen molecules in excess argon will be described.

Mg + O_2. The spectra in Figure 1 are typical of several natural isotopic experiments. Codeposition of pulsed laser produced Mg
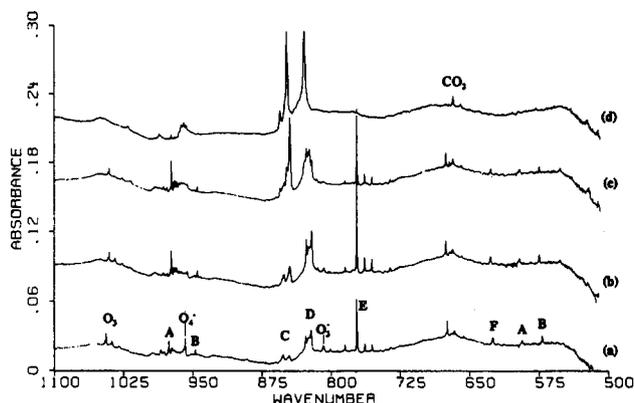
Figure 1. Infrared spectra in the 1100–500-cm⁻¹ region for pulsed laser evaporated Mg atoms and 1% O_2 in argon at 10 K: (a) sample codeposited for 3 h, (b) after photolysis for 30 min, (c) after annealing to 25 ● 2 K, and (d) after annealing to 35 ± 2 K.

atoms, and 1% O_2 in argon (Figure 1a) produced weak familiar absorptions at 1039.5, 1033.0, (O_3), 953.9, (O_4^-), and 803.9 cm⁻¹ (O_3^-).[14-16] New absorptions were observed at 971.7 and 943.1 cm⁻¹ (labeled A and B), 847.9, 841.3 cm⁻¹ (labeled C), and 823.2, 817.6 cm⁻¹ (labeled D) in this region. The sharp strong band at 767.7 cm⁻¹ and satellites at 759.0 and 750.9 cm⁻¹ (labeled E) with 7:1:1 relative intensity are of particular interest. The 669.9-cm⁻¹ band was observed in previous ozone experiments and assigned to a Mg_xO_y species; owing to CO_2 impurity in this region, no new information was obtained here.[7] Weak new bands were observed in the lower frequency region at 621.1, 591.7, and 567.2 cm⁻¹ (labeled F, A, and B). Photolysis with the full light of a medium-pressure mercury arc caused substantial changes (Figure 1b); the O_3, O_4^-, and O_3^- absorptions decreased, and the A, B, C, and D absorptions increased slightly. Of most interest, the E band increased by 100%, and the F band increased slightly. A weak band at 730.8 cm⁻¹ also increased on photolysis. Annealing to 25 ± 2 K to allow diffusion and reaction of trapped species (Figure 1c) markedly increased the 841.3-cm⁻¹ C band and slightly increased the A and B bands and decreased other features. Annealing to 30 ± 2 K (not shown) decreased the E and F bands further. Finally, annealing to 35 ± 2 K (Figure 1d) left a broad 956-cm⁻¹ band in the upper region, further increased C and D site absorptions at 844.7 and 823.2 cm⁻¹ bands, markedly reduced the E bands, and destroyed the remaining absorptions.

An experiment with 0.5% O_2 in argon and higher laser power gave sharper product bands, increased yields, particularly of A and B bands, and provided further evidence for association of the upper and lower frequency A and B bands by their 50% growth on photolysis. The 866.9- and 730.8-cm⁻¹ bands from previous ozone experiments[7] were also detected.

TABLE I: Infrared Absorptions (cm⁻¹) Observed for Pulsed Laser Ablated Magnesium Atom Reactions with Oxygen Molecules during Condensation in Excess Argon

| $^{26}Mg + {}^{16}O_2$	$^nMg + {}^{16}O_2$	$^nMg + {}^{18}O_2$	identity
1039.5	1039.5	982.3	O_3
1033.0	1033.0	976.3	O_3
966.4	980.4	941.3	A site
959.7	971.7	935.3	A, MgOMgO
953.9	954.0	901.9	O_4^-
931.9	943.1	906.9	B, MgOMgO
	866.9		G, (OMgO) complex
	847.9	801.7	C, MgO_3
840.3	841.3	796.6	C, MgO_3
823.0	823.2	777.8	D, MgO_3
816.8	817.6	772.1	D, MgO_3
812.8			MgO
804.0	803.9	759.2	O_3^-
	780.5		?
750.9	771.9	753.7	E site
	767.7	749.5	E, OMgO
750.9	759.0	740.6	E, OMgO
	750.9	732.2	E, OMgO
714.8	730.8	713	$MgO\cdot O_2$
652.3	669.9		Mg_xO_y
608.5	621.1	604.4	F, MgO_2
582.3	591.7	574.8	A, MgOMgO
556.7	567.2	551.0	B, MgOMgO

Mg + $^{18}O_2$. Pulsed laser evaporated magnesium atoms and $^{18}O_2$ produced a similar spectrum with appropriate isotopic shifts; the band positions are given in Table I. Photolysis had the same effect on the spectrum: the A, B, C, D, E, and F bands increased substantially. Annealing to 30 ± 2 K increased the C and D bands and decreased the E and F absorptions.

Mg + $^{16,18}O_2$. One experiment was done with scrambled isotopic oxygen, and the spectrum is shown in Figure 2. The A and B bands give apparent mixed isotopic doublets, but the bands are broadened and shifted slightly from the pure isotopic values. The A components were observed at 971.0 and 936.0 cm⁻¹ and the B components at 942.5 and 907.4 cm⁻¹ in the scrambled isotopic experiments. Mixed isotopic D bands were observed at 808.0 and 783.3 cm⁻¹. The spectrum was dominated by a sharp E band triplet at 767.7, 759.1, and 749.5 cm⁻¹; a weak triplet was observed at 621.1, 613.6, and 604.4 cm⁻¹ in the lower region, but the weaker lower frequency A and B bands were not observed. Photolysis with a Pyrex filter (not shown) increased the A and B bands and the F triplet by 30%. Photolysis with the full arc increased the A bands, decreased B, increased D, and increased E by 30% more (Figure 2b). Annealing had the same effect as in the pure isotopic samples (Figure 2c).

$^{26}Mg + O_2$. Atoms evaporated from a ^{26}Mg target and codeposited with 1% O_2 in argon for 4 h gave a similar spectrum with product bands shifted as listed in Table I; an additional weak band was observed at 812.8 cm⁻¹. The strongest E band at 750.9 cm⁻¹ corresponds to one of the E band satellites from natural isotopic magnesium. Annealing to 30 K increased A and decreased B, markedly increased the C and D bands, and decreased the E, F, and 812.8-cm⁻¹ absorption.

Mg + N_2O. Several complementary experiments were done with magnesium atoms and 1% N_2O in argon. These experiments produced weak 1039.5, 1033.0 (O_3), and 803.6-cm⁻¹ (O_3^-) bands, but the band in the D region now peaked at 825.5 cm⁻¹. In addition, a broad band ranging from 975 to 925 cm⁻¹ with sharp A and B peak substructure, a weak G band at 866.9 cm⁻¹, a weak E band at 767.7 cm⁻¹, and a stronger new band at 760.2 cm⁻¹ were observed as listed in Table II. With ^{26}Mg the latter bands shifted to 848.4, 750.9, and 743.4 cm⁻¹, the broad band with A and B peak substructure shifted 11 cm⁻¹ lower, the D band peaked at 823.4 cm⁻¹, and a new band was observed at 812.8 cm⁻¹. For both Mg isotopes annealing to 25 K decreased the sharp bands and produced a strong common 827.1-cm⁻¹ absorption.

MgO Pellets. Three experiments were done using pressed MgO
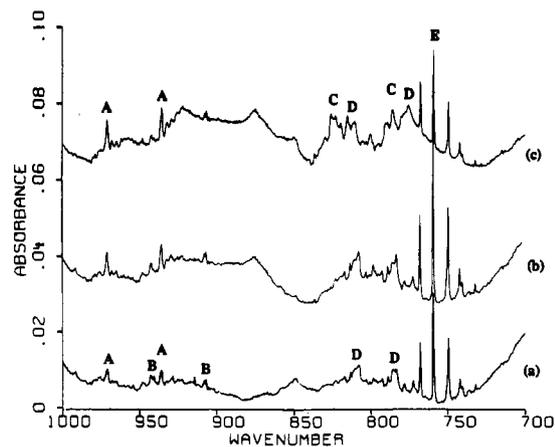
Figure 2. Infrared spectra in the 1000–700-cm⁻¹ region for pulsed laser evaporated Mg atoms and 1% O_2 in argon using $^{16}O_2/{}^{16}O^{18}O/{}^{18}O_2$ isotopic mixture: (a) sample codeposited for 3 h, (b) after photolysis for 30 min, and (c) after annealing to 30 ± 2 K.

TABLE II: Infrared Absorptions (cm⁻¹) Observed for Pulsed Laser Ablated Magnesium Atom Reactions with N_2O in Excess Argon

$^nMg + N_2O$	$^{26}Mg + N_2O$	identity
1039.5	1039.5	O_3
1033.0	1033.0	O_3
971.7[a]	959.7[a]	A, MgOMgO
943.1[a]	931.9[a]	B, MgOMgO
	905	?
866.9	848.4	G, (OMgO) complex
825.5	812.8	MgO
b	823.4	D, MgO_3
803.6	803.6	O_3^-
767.7	750.9	E, OMgO
760.2	743.4	(OMgO)(N_2) complex

[a] Structure on broad underlying band. [b] Masked.
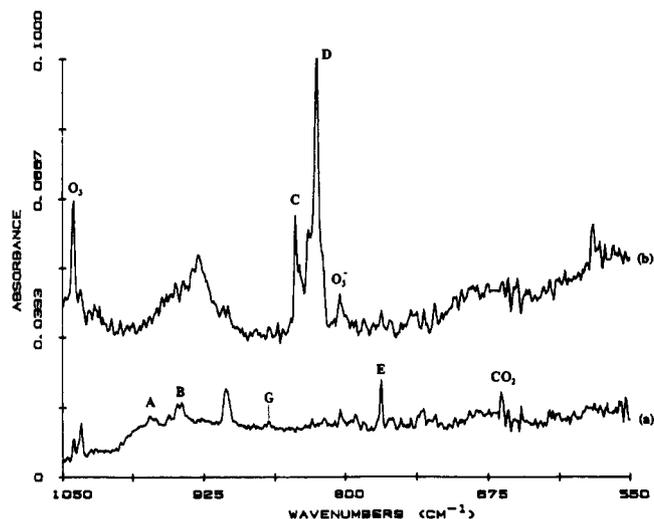
Figure 3. Infrared spectra in the 1050–550-cm⁻¹ region for pulsed laser ablated fused MgO codeposited with excess argon at 10 K: (a) sample codeposited for 2 h and (b) after annealing to 30 ± 2 K.

pellets as laser targets, and the ablated products were collected in an argon matrix. Sharp medium-intensity bands were observed at 1039.5, 1033.0 (O_3), 866.9 (G), and 767.7 cm⁻¹ (E), sharp weak bands were detected at 980.0, 971.8 (A), 943.2 (B), and 719.0 cm⁻¹, and a new band appeared at 906 cm⁻¹. In addition, weak HO_2, CO_2, and H_2O absorptions[17] were observed. Annealing to 30 K decreased the sharp bands and produced a new D band at 824 cm⁻¹. A similar experiment collected the species ablated from MgO in an Ar/O_2 = 100/1 matrix. The 980.4-, 971.7-, and 767.7-cm⁻¹ bands were double their intensity above, and the 823.2-

TABLE III: Observed Anharmonic and Calculated Harmonic Ratios for Antisymmetric Stretching Fundamentals of Linear O–Mg–O Isotopic Molecules

isotopes	16–24–16/18–24–18	16–24–16/16–25–16	16–24–16/16–26–16	16–26–16/18–26–18	18–24–18/18–25–18	18–24–18/18–26–18
obsd	1.024 28	1.011 46	1.022 37	1.025 54	1.012 02	1.023 63
calcd	1.024 74	1.011 58	1.022 68	1.025 92	1.012 17	1.023 86

and 730.8-cm^{-1} bands were clearly observed on sample deposition. The 866.9-cm^{-1} band, however, was halved. In addition, ozone was increased 10-fold, and O_3^- was detected. Annealing had the same effect as discussed above; the sharp bands decreased, and the ozonide band increased markedly at 824.7 cm^{-1}.

Three experiments were done with a fused MgO target, and a spectrum is shown in Figure 3a. Note the sharp A and B bands, a new 906-cm^{-1} absorption, and the sharp E band. Annealing to 30 K, Figure 3b, increased O_3 and produced a new pair of bands at 929.5 and 583.2 cm^{-1} and the strong C and D bands. Photolysis in a different fused MgO experiment increased the 971.7- and 591.7-cm^{-1} A bands at the expense of the 943.1- and 567.2-cm^{-1} B bands.

Discussion

The product bands unique to pulsed laser experiments will be identified, and reaction mechanisms will be discussed.

Linear OMgO. The sharp new product band at 767.7 cm^{-1} (labeled E) dominates the pulsed laser experiments. Furthermore, this band increases markedly (doubles) on broad-band photolysis. Isotopic data clearly demonstrate that one Mg and two equivalent oxygen atoms are present in this species. The 7:1:1 triplet with natural isotopic Mg (78.7% ^{24}Mg, 10.1% ^{25}Mg, 11.2% ^{26}Mg) (Figure 1) is indicative of a single Mg atom, and observation of only the latter band with a ^{26}Mg target confirms the isotopic assignment. The 1:2:1 triplet with statistical isotopic $^{16,18}O_2$ (Figure 2) shows that two equivalent oxygen atoms are involved; only the former and the latter components were observed with pure $^{16}O_2$ and pure $^{18}O_2$.

The observed isotopic ratios are in excellent agreement with ratios predicted for the antisymmetric stretching fundamental of a linear harmonic O–Mg–O oscillator from vibrational analysis. Table III shows that the observed anharmonic ratios (1.024 28 for 16/18) are slightly lower than the calculated harmonic ratios (1.024 74) as appropriate for cubic contributions to anharmonicity. This agreement demonstrates that O–Mg–O is a linear molecule. Furthermore, valence angle calculations from isotopic ν_3 fundamentals[18] predict an upper limit cosine of -1.06 and a lower limit cosine of -0.94 for the O–Mg–O valence angle, which average to the limit for a linear molecule. In view of the approximations involved, these calculations based on the observed matrix data confirm that the sharp 767.7-cm^{-1} argon matrix absorption is due to linear O–Mg–O.

High-level quantum chemical calculations by Bauschlicher et al. have predicted that the linear $^3\Sigma_g^-$ O–Mg–O molecule is slightly (3 kcal/mol) lower in energy than the cyclic $^3A_2$ MgO$_2$ species.[13] Furthermore, the ν_3 fundamental predicted by ab initio calculations for linear OMgO at 796 cm^{-1} is in excellent agreement with the 767.7-cm^{-1} argon matrix value reported here. Since O–Mg–O has no dipole moment, the calculated and argon matrix values are expected to closely approximate the still unobserved gas-phase value. Finally, the excellent agreement between theoretical and matrix ν_3 values for linear OMgO confirms the observation of this species. The central component at 759.1 cm^{-1} for ^{16}O–Mg–^{18}O in the mixed oxygen isotopic triplet is 0.5 cm^{-1} above the average of the 767.7- and 749.5-cm^{-1} values for ^{16}O–Mg–^{16}O and ^{18}O–Mg–^{18}O, respectively. This points to a lower symmetric stretching fundamental, calculated[13] at 533 cm^{-1}. In the ^{16}O–Mg–^{18}O isotopic molecule of lower symmetry, interaction between the two stretching modes forces the antisymmetric stretching mode slightly higher.

Cyclic MgO$_2$. Theoretical calculations[13] predicted strong ν_2 (symmetric Mg–O) and weak ν_3 (antisymmetric Mg–O) fundamentals for cyclic MgO$_2$ (O–Mg–O angle $= 40°$) at 540 and 406 cm^{-1}. Cyclic MgO$_2$ has a substantial dipole moment, and both calculated and observed matrix values may accordingly depart from the ideal gas-phase value. The 681- and 426-cm^{-1} nitrogen matrix values assigned earlier[7] to cyclic MgO$_2$ exhibit isotopic ratios with more Mg and less O participation than a harmonic diatomic vibration. In fact, a cyclic MgO$_2$ species with a O–Mg–O angle near 40°, that calculated[13] for $^3A_2$ cyclic MgO$_2$, exhibits ν_2 and ν_3 fundamentals with the observed isotopic ratios. This assignment was questioned on the basis of somewhat higher values than predicted by quantum chemical calculations.[13] However, the large blue shift ($+53$ cm^{-1}) observed for MgO in solid nitrogen[7] suggests a large blue shift for likewise ionic Mg$^+$O$_2^-$ species. Furthermore, the quantum chemical calculations may be subject to some error owing to the substantial ionicity in cyclic MgO$_2$. Hence, the original cyclic MgO$_2$ observation in solid N$_2$, supported by oxygen and magnesium isotopic data, is still believed to be correct.

Where, then, will cyclic MgO$_2$ absorb in solid argon? Probably closer to the gas-phase fundamental, which, based on theory, is expected to be lower in frequency. The present F band at 621.1 cm^{-1} exhibits a mixed oxygen isotopic triplet for two equivalent oxygen atoms. The 16/18 isotopic ratio 621.1/604.4 = 1.027 63 is less than the harmonic diatomic value (1.035 17), and the 24/26 isotopic ratio 621.1/608.5 = 1.020 71 is greater than the diatomic value (1.015 72). These ratios are also in accord with that expected for ν_2 of cyclic MgO$_2$ with a valence angle near 40°. The 621.1-cm^{-1} band is tentatively assigned to cyclic MgO$_2$ in solid argon. It is suggested that the gas-phase cyclic MgO$_2$ fundamental will be in the 580–600-cm^{-1} range. Large matrix interactions and shifts are appropriate for ionic molecules.

Linear MgOMgO. The A and B bands increase slightly on photolysis, and the A bands grow on annealing often accompanied by a decrease in the B bands. The higher frequency A and B bands exhibit 16/18 ratios (1.038 92 and 1.039 92, respectively) that are slightly higher than the harmonic diatomic ratio (1.035 17), whereas these bands exhibit 24/26 ratios (1.012 50 and 1.012 02, respectively) that are lower than the harmonic diatomic ratio (1.015 72). Clearly, the upper A and B vibrations involve *more* O and *less* Mg motion than a harmonic MgO fundamental vibration. On the other hand, the lower-frequency A and B bands give 16/18 ratios (1.029 40 and 1.029 40) that are lower and 24/26 ratios (1.016 14 and 1.018 86, respectively) that are higher than the harmonic diatomic ratios. Clearly, the lower A and B bands involve *less* O and *more* Mg participation than a pure MgO fundamental. This is reminiscent of the linear AlOAlO molecule, which exhibits two strong Al–O vibrations with analogous atomic vibrational participations.[3] The A and B bands behave appropriately for the linear dimer MgOMgO. Furthermore, the mixed oxygen isotopic stronger upper bands are consistent with a quartet containing 16–18 components displaced 1 cm^{-1} from the pure isotopic components, which denotes the vibration of one oxygen atom weakly coupled to a second inequivalent oxygen atom. Unfortunately, the A and B bands were not strong enough to observe a magnesium isotopic multiplet in natural abundance. However, an increase in the A and B bands relative to the linear OMgO band when the Mg/O$_2$ ratio was increased suggests that the A and B absorbers contain two Mg atoms. Species A and B are therefore identified as MgOMgO species in different matrix sites or with slightly different structures.

The stronger A and B bands were also observed in MgO pellet and Mg + N_2O ablation experiments and in the thermal Mg + O_3 argon matrix experiments reported earlier.[7] Annealing in fused MgO target experiments produced another analogous pair of bands at 929.5 and 583.2 cm^{-1} for a third MgOMgO matrix site. Although these bands appear in the region of $M^+O_4^-$ absorptions,[16] the large magnesium isotopic shift (11–12 cm^{-1}) and the medium oxygen isotopic shift (34–36 cm^{-1}) show that this a perturbed Mg–O vibration and not an O–O motion. All of these experiments are expected to produce MgO, and the dimer MgOMgO is a likely product.

Preliminary calculations on MgOMgO have been done at the SCF level and the 6-31G* basis set using the ACES II program system[19] in order to assist in assigning of the matrix spectra. Although ab initio calculations have been performed for MgO at the CI level,[20] no ground-state frequency was reported, and the MgO calculation was repeated here as a standard of comparison for MgOMgO. Values calculated here for MgO include $E(SCF)$ = –274.3238 hartrees, r = 1.738 Å, ω = 768 cm^{-1} (116 km/mol), and μ = 7.87 D. The bond length and frequency compare very favorably to experimental data (1.749 Å and 775 cm^{-1}).[21]

Values calculated for the linear Mg–O–Mg–O molecule include $E(SCF)$ = –548.7759 hartrees, 1.7193, 1.8548, and 1.7513 Å bond lengths, and 961.2 cm^{-1} (1470 km/mol), 811.2 cm^{-1} (2230 km/mol), 406.9 cm^{-1} (13 km/mol), and 190.5 cm^{-1} (2 × 163 km/mol) frequencies. The first frequency is essentially a terminal Mg ↔ O– vibration, and the second is due primarily to the other –Mg ↔ O stretching mode. The calculated 961.2-cm^{-1} fundamental is between the upper A and B bands, whereas the 811.2-cm^{-1} prediction is somewhat higher than the lower A and B bands. The calculated isotopic ratios, *which define the normal mode*, however, are in very good agreement with the observed ratios (calculated for 16/18, 961.2/922.3 = 1.042 18 and 811.2/788.9 = 1.028 27; calculated for 24/26, 961.2/950.8 = 1.010 94 and 811.2/795.3 = 1.019 99). Furthermore, the Mg-16–Mg-18 and Mg-18–Mg-16 isotopic frequency calculations predict the small (1 cm^{-1}) splitting observed from the Mg-16–Mg-16 and Mg-18–Mg-18 isotopic species. In conclusion, the above SCF calculations for MgOMgO predict the vibrational spectrum reasonably well and strongly support the present identification of linear MgOMgO. A higher level calculation is expected to produce better frequency agreement. Note that $E(SCF)$ for MgOMgO is 80 kcal/mol lower than $2E(SCF)$ for MgO, and accordingly MgOMgO is a stable dimer species, as suggested by the present matrix experiments. Finally, there was no evidence for a cyclic $(MgO)_2$ species in these experiments.

MgO_3 Species. The C and D bands were produced in the earlier reaction of Mg and O_3 and assigned to $Mg^+O_3^-$ species.[7] Similar absorptions were also formed in the reaction of Mg and discharged O_2, and these bands have been reassigned to $Mg^+O_3^-$.[7,22] The isotopic shifts observed here are in agreement with and support the earlier assignments.[7] Since very little O_3 was observed in the present experiments, the $Mg^+O_3^-$ species probably arise from the reaction of MgO and O_2 in these experiments. In this regard, the very weak band at 730.8 cm^{-1} observed in both Mg + O_2 and MgO + O_2 experiments is in accord with a major product in the O_3 experiments identified as MgO–O_2.[7]

Other Absorptions. There remain several weak absorptions to be identified. The 866.9-cm^{-1} band (labeled G) is a minor product in MgO pellet experiments, the present Mg + O_2, Mg + N_2O, and earlier thermal Mg + O_3 experiments.[7] The magnesium isotopic ratio 866.9/848.4 = 1.0218 is slightly lower than the value for linear OMgO, and since OMgO is a major product in the MgO pellet experiments, the 866.9-cm^{-1} band is assigned to complexed OMgO. The ground-state OMgO molecule exhibits a substantial positive charge on the central magnesium atom,[13] and complexation with another molecule is expected to be favorable. Possibilities in the MgO pellet experiments include

H_2O and MgO itself. The 760.2-cm^{-1} band in N_2O experiments likewise exhibits a magnesium isotopic ratio 760.2/743.9 = 1.0226 near that for linear OMgO. Proximity to the 767.7-cm^{-1} OMgO band and the ready availability of N_2 in the reaction mechanism indicate that the 760.2-cm^{-1} band is due to OMgO weakly perturbed by N_2. The sharp weak bands at 719.0 cm^{-1} in the pressed MgO pellet experiment fall below the 750-cm^{-1} value reported for MgOH in the gas phase.[23] In addition, the MgOH molecule has been characterized by matrix ESR experiments.[24] The present 719.0-cm^{-1} band is tentatively assigned to MgOH produced by pulsed laser decomposition of $Mg(OH)_2$ on the pellet surface. A 25–31-cm^{-1} red matrix shift for the Mg–OH vibrational fundamental is reasonable.

Finally, where does MgO absorb in solid argon? This molecule also possesses a substantial positive charge at magnesium[20] and is expected to undergo a significant matrix shift and to complex readily with other molecules. The similar molecule BeO, which also has a large dipole moment, forms a strong complex with Ar, based on quantum chemical calculations.[25] In fact, MgO has been identified in solid N_2 at 828.3 cm^{-1}, blue-shifted by 53 cm^{-1} from the 775-cm^{-1} gas-phase fundamental.[7] Furthermore, the 799.0-cm^{-1} MgO_3 species identified earlier[7] also has substantial Mg–O stretching character and might be better described as O_2–MgO. It appears that MgO probably absorbs in the MgO_3 region in solid argon as found in solid nitrogen. In the N_2O experiments, which had the highest yield of MgOMgO, the "MgO_3 band" peaked at 825.5 cm^{-1} for ^nMg and at the normal 823.4-cm^{-1} position for ^{26}Mg where a new band appeared at 812.8 cm^{-1}. A weak 812.8-cm^{-1} band was also observed with ^{26}Mg and O_2. The 825.5/812.8 = 1.015 63 ratio is in excellent agreement with the harmonic ratio for MgO and supports this identification of MgO in solid argon.

Reaction Mechanisms. The primary reaction (1) of Mg and

$$Mg + O_2 \rightarrow O\text{–}Mg\text{–}O \qquad (1)$$
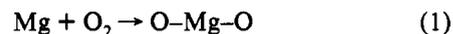
O_2 is exothermic by some 26 kcal/mol and has an activation energy near 12 kcal/mol based on calculations.[12,13] Clearly, this reaction will not proceed on condensation of thermal reagents in excess argon, as has been demonstrated in this laboratory.[6] However, pulsed laser ablated metal atoms are known to possess considerable excess kinetic energy. Under similar conditions an average kinetic energy near 5 eV has been measured for pulsed laser ablated aluminum atoms,[26] and such atoms undergo insertion to give OAlO on condensation in excess argon.[3] Similar kinetic energies for the present pulsed laser evaporated Mg atoms provide the activation energy necessary for reaction 1. In addition, the co-condensation process allows unreacted $(Mg)(O_2)$ pairs to be trapped in the matrix. Irradiation into the strong atomic Mg $^1P_1$ ← $^1S_0$ resonance absorption at 270–290 nm in solid argon[27,28] produced a marked growth in the OMgO absorption (Figure 1). It must be concluded that excited $^1P_1$ (3s3p) Mg atoms spontaneously insert to give linear OMgO. The cyclic $MgO_2(^3A_2)$ species has been calculated about 3 kcal/mol higher in energy than linear OMgO.[13] It is certainly reasonable for a small amount of cyclic MgO_2 to be formed in the relaxation of the product of reaction 1.

Previous gas-phase studies have shown reaction 1 to be slow, but a 3-fold rate increase has been observed with N_2 as compared to He carrier gas.[12] A similar reactivity enhancement has been found in matrix reaction studies. Both O_2 and O_3 are more reactive with Mg on condensation with excess N_2 than with excess argon.[7] In particular, reaction 1 gave no products on condensation with excess argon,[6] but using nitrogen allowed MgO_3 and bands presently identified as MgOMgO to be observed.[7] A similar enhancement of reactivity for Li atoms with N_2O and O_3 has been found for N_2 as compared to Ar as the carrier gas or matrix environment.[29] Molecular nitrogen is known to interact more strongly with ionic species than argon, and the reaction rate

increase follows accordingly. Finally, it is interesting to contrast the relative yields of linear O–Mg–O and cyclic MgO_2 in the earlier Mg + O_3 reactions using argon and nitrogen carrier gases. In argon a trace of O–Mg–O and no MgO_2 was observed; however, in nitrogen no O–Mg–O and a substantial amount of cyclic MgO_2 was produced. The role of nitrogen in stabilizing polar species is again demonstrated.

The abstraction reaction (2) is considerably endothermic (31–

$$Mg + O_2 \rightarrow O + MgO \qquad (2)$$

57 kcal/mol) with uncertainty depending on the estimate for $D(\text{Mg–O})$.[12] Although no direct evidence for MgO has been found in the O_2 experiments, the observation of magnesium ozonide (C and D absorptions) most likely involves MgO in reaction 3.

$$MgO + O_2 \rightarrow MgO_3 \text{ (i.e., } Mg^+O_3^-) \qquad (3)$$
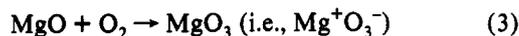
The MgOMgO species is, of course, a dimer of MgO, but in the present O_2 experiments MgOMgO is most probably formed in the secondary reaction 4. Even with hyperthermal Mg atoms, the yield of MgO in the present experiments is very low, and most of the MgO produced probably reacts with O_2 by reaction 3.

$$Mg + OMgO \rightarrow MgOMgO \qquad (4)$$

The Mg reaction with N_2O (5) gives MgO with threshold energies in the 7–9 kcal/mol range as measured using pulsed laser evaporation.[30] Reaction 5 is expected to be faster than reaction 2, and the higher yield of MgO and MgOMgO in N_2O experiments follows.

$$N_2O + Mg \rightarrow N_2 + MgO \qquad (5)$$

The observation of OMgO suggests that MgO can also abstract an oxygen atom from N_2O. The belated discovery that OMgO was a trace product in the earlier argon/ozone experiments[7,31] is also consistent with reactions 5 and 6 where ozone replaces nitrous oxide.

$$N_2O + MgO \rightarrow N_2 + OMgO \qquad (6)$$

Finally, what role do Mg^+ ions play in these experiments? The focused pulsed laser probably evaporates some Mg^+ cations and electrons as well as Mg atoms. The trapping of electrons is documented by detection of the strongly absorbing isolated O_4^- and O_3^- anions in the spectrum.[14–16] Although the presence of MgO_x^+ molecular ions in these samples cannot be ruled out, no case can be made for their characterization. Most of the charged species that reach the matrix probably recombine to form neutral species. The dominant species produced and trapped in these experiments are neutral molecules.

Conclusions

Pulsed laser ablated Mg atoms insert into molecular oxygen to give the linear O–Mg–O molecule calculated to be the ground state. Magnesium and oxygen isotopic multiplets and shifts in the antisymmetric stretching fundamental verify the stoichiometry and the linear structure. Further reaction with Mg gives the linear Mg–O–Mg–O molecule, which is characterized by two

Mg–O stretching modes. Most of the low yield of MgO in these experiments is consumed by O_2 to form magnesium ozonide; however, similar studies with N_2O gave an increased yield of MgOMgO and evidence for MgO in solid argon. Finally, pulsed laser ablated Mg atoms possess sufficient kinetic energy to activate the reaction with O_2 in argon carrier gas whereas thermally evaporated Mg atoms do not react under the conditions of these experiments.

References and Notes

(1) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8679.
(2) Andrews, L.; Burkholder, T. R. *J. Phys. Chem.* **1991**, *95*, 8554.
(3) Andrews, L.; Burkholder, T. R.; Yustein, J. T. *J. Phys. Chem.* **1992**, *96*, 10182.
(4) Zehe, M. J.; Lynch, Jr., D. A.; Kelsall, B. J.; Carlson, K. D. *J. Phys. Chem.* **1979**, *83*, 656.
(5) Burkholder, T. R.; Yustein, J. T.; Andrews, L. *J. Phys. Chem.* **1992**, *96*, 10189.
(6) Andrews, L. Unpublished results, 1968–1978.
(7) Andrews, L.; Prochaska, E. S.; Ault, B. S. *J. Chem. Phys.* **1978**, *69*, 556.
(8) Hodgson, A.; Mackie, J. C. *Combust. Flame* **1979**, *35*, 323.
(9) Kashireninov, O. E.; Manelis, G. B.; Repka, L. F. *Zh. Fiz. Khim.* **1982**, *56*, 1030; *Russ. J. Phys. Chem.* **1982**, *56*, 630.
(10) Plane, J. M. C. In *Gas-Phase Metal Reactions*; Fontijn, A., Ed.; Elsevier: Amsterdam, 1992.
(11) Vinckier, C.; Christiaens, P.; Hendrickx, M. In *Gas-Phase Metal Reactions*; Fontijn, A., Ed.; Elsevier: Amsterdam, 1992.
(12) Nein, C.-F.; Rajasekjhar, B.; Plane, J. M. C. *J. Phys. Chem.* **1993**, *97*, 6449.
(13) Bauschlicher, Jr., C. W.; Partridge, H.; Sodupe, M.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 9259.
(14) Andrews, L.; Spiker, Jr., R. C. *J. Phys. Chem.* **1972**, *76*, 3208.
(15) Spiker, R. C., Jr.; Andrews, L. *J. Chem. Phys.* **1973**, *59*, 1851. Andrews, L.; Ault, B. S.; Grzybowski, J. M.; Allen, R. O. *J. Chem. Phys.* **1975**, *62*, 2461.
(16) Andrews. L. *J. Chem. Phys.* **1971**, *54*, 4935. Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **1989**, *91*, 3826. Hacaloglu, J.; Andrews, L. To be published.
(17) Smith, D. W.; Andrews, L. *J. Chem. Phys.* **1974**, *60*, 81. Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1963**, *38*, 2627.
(18) Allavena, M.; Rysnik, R.; White, D.; Calder, V.; Mann, D. E. *J. Chem. Phys.* **1969**, *50*, 3399.
(19) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. ACESII, Quantum Theory Project, University of Florida, Gainesville, FL, 1992.
(20) Langhoff, S. R.; Bauschlicher, Jr., C. W. *J. Chem. Phys.* **1986**, *84*, 4474.
(21) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1979.
(22) Spoliti, M.; Marini, G.; Cesaro, S. N.; DeMaria, G. *J. Mol. Struct.* **1973**, *19*, 563.
(23) Bauschlicher, Jr., C. W.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 901.
(24) Brom, J.; Weltner, Jr., W. W. *J. Chem. Phys.* **1973**, *58*, 3322.
(25) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007.
(26) Wang, H.; Salzberg, A. P.; Weiner, B. R. *Appl. Phys. Lett.* **1961**, *59*, 935.
(27) Schnepp, O. *J. Phys. Chem. Solids* **1961**, *17*, 188.
(28) Knight, Jr., L. B.; Ebener, M. A. *J. Mol. Spectrosc.* **1976**, *61*, 412.
(29) Spiker, Jr., R. C.; Andrews, L. *J. Chem. Phys.* **1973**, *58*, 702; **1973**, *59*, 1851.
(30) Costes, M.; Naulin, C.; Moudden, Z.; Dorthe, G. *J. Phys. Chem.* **1991**, *95*, 8244.
(31) OMgO was a trace product in the Mg + Ar/O_3 experiments described in ref 7 as can be seen from the unassigned 732.5-cm^{-1} band in Table II and Figure 4d for the 18–26–18 isotopic molecule.