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PROPOSED LETTER TO THE EDITOR

FORMATION OF CO_2^- RADICAL IONS WHEN CO_2 IS ADSORBED

ON IRRADIATED MAGNESIUM OXIDE

by Jack H. Lunsford and John P. Jayne

Lewis Research Center
Cleveland, Ohio

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Introduction

The application of electron paramagnetic resonance (EPR) spectroscopy to adsorbed molecules has proved the existence of certain radical species that may be intermediates in chemical reactions. The early studies were primarily on adsorbed polynuclear organic compounds.[1-3] An investigation of oxygen on zinc oxide has been reported;[4] however, the particular oxygen radical was not conclusively identified. The formation of surface paramagnetic centers by γ-irradiation of degassed MgO has been recently reported by Nelson and Tench.[5] This type of center, termed an S center, is thought to be an electron trapped at a surface anion vacancy. The S centers as well as a reddish-blue color are rapidly destroyed upon exposure to oxygen. We have observed a similar phenomenon with MgO following ultra-violet irradiation and, in addition, have observed the spectrum of an oxygen radical ion that is formed on adsorption. This is to be reported separately.[6] It was of interest to see if other gases would also form radical ions when adsorbed on the irradiated surface. In the work reported here we have observed the EPR spectrum of CO_2 adsorbed on ultraviolet-irradiated MgO. The spectrum of adsorbed CO_2 is compared with the EPR spectrum of the CO_2^- radical ion that Ovenall and Whiffen[7] have analyzed in some detail.

Experimental

The MgO used in this experiment was prepared from reagent grade powder. Most of the data were taken on samples that had been impregnated with 0.0035 percent Fe as $FeCl_3$ or $Fe(NO_3)_3$ and on the original powder that contained about 0.0010 percent Fe. The powder was boiled in water for several hours, extruded into pellets with a hypodermic syringe, and dried in air at 100° C. Degassing was carried out by heating the pellets to 800° C in a vacuum for several hours. All the samples were then irradiated for 16 hr by using a low pressure mercury lamp with an intensity of 60 $\mu W/cm^2$ at 2537 A.

Electron paramagnetic resonance data were obtained with a Varian spectrometer operating at a cavity resonance frequency of 9100 Mc/sec. A nuclear magnetic resonance (NMR) type gaussmeter was used to monitor the magnetic field continuously. The g-values were obtained by comparison with the value for α,α-diphenyl β-picryl hydrazyl (DPPH) that was placed on the outside of the quartz tube containing the MgO sample. The g-value of the DPPH was taken as 2.0036.

After ultraviolet irradiation, the sample was checked for the paramagnetic center and the violet color. When these were present, CO_2 was admitted to the sample at a pressure of about 100 torr and at room temperature. A mixture of 57 percent $C^{13}O_2$ and 43 percent $C^{12}O_2$ was adsorbed on several samples in an effort to observe the C^{13} hyperfine spectrum that could be used to identify the radical species. The mixture was purified by freezing the CO_2 at 77° K and pumping off any residual oxygen.

Spectra were also obtained for unirradiated MgO that had been degassed and exposed to CO_2.

Results

After several hours of ultraviolet irradiation the violet color of the sample begins to appear, and the EPR spectrum shown in Fig. 1 was observed. This spectrum of the center, which we will designate an S' center, has the g-values shown in the figure and listed in Table I. The EPR transition can be saturated with a moderate amount of microwave power (approximately 3 mW). The paramagnetic species is fairly stable through 100° C, but heating to 200° C for 30 min reduces the intensity of the derivative curve by 90 percent. It was further observed that the intensity of the spectrum was enhanced by a factor of 2 by adding the 0.0035 percent Fe as $FeCl_3$ or $Fe(NO_3)_3$.

Upon exposure to CO_2, both the S' center spectrum and the violet color disappear, and the new derivative spectrum shown in Fig. 2 appears. The g-values of this new spectrum was also listed in Table I. Adsorption of CO_2 enriched to 57 percent C^{13} results in two rather broad hyperfine lines symmetrically disposed on each side of the $C^{12}O_2^-$ spectrum. The amplitude of the hyperfine lines is less than one-tenth of the amplitude of the central line, which is associated with the 47 percent $C^{12}O_2$. Values for the hyperfine coupling constants are listed in Table II.

The S' center is destroyed by a partial pressure of oxygen in the CO_2 as low as 10^{-3} torr, and no CO_2 spectrum can be detected. One can regenerate the S' center, however, by again heating the sample to 800° C in vacuum and irradiating with ultraviolet light.

Discussion

Ultraviolet light with an energy of 4.9 eV apparently promotes electrons into traps that exist on the surface of the degassed MgO. The re-

sulting EPR spectrum, shown in Fig. 1, is characteristic of a center having rhombic symmetry. The similarity in the g-value of the S' center to the g-value of the S center[5] and the annealing behavior of the centers indicate that they are related; that is, both centers are electrons trapped at a surface defect. The S center, however, does not have rhombic symmetry. If the S' center was an electron trapped at an anion-cation vacancy pair existing in the plane of the surface, rhombic symmetry would be satisfied. One symmetry axis would be along the vacancy pair and the other axis would be perpendicular to the surface. It should be pointed out that the bulk F_2 center (an electron trapped at an anion-cation vacancy pair) reported by Wertz, et al.[8] has a g-value of 2.0008 ± 0.0002 and a fairly long relaxation time. We shall assume for this paper that the irradiation-induced paramagnetic center on the surface of the MgO is an electron trapped at an anion-cation vacancy pair in the plane of the surface. The concentration of the cation vacancies is undoubtedly enhanced by the trivalent iron ion through charge compensation,[9,10] but the mechanism by which the anion vacancies are formed is not presently known.

A comparison of the g-values for the spectrum of CO_2 adsorbed on ultraviolet irradiated MgO with the spectrum of CO_2^- radical ions in γ-irradiated sodium formate (NaCOOH) single crystals shows that within experimental error there is complete agreement. As a result of the similarity in the spectra and the analysis by Ovenall and Whiffen of the structure of the CO_2^- radical ion, we conclude that CO_2 adsorbs on irradiated MgO as a planar radical ion shown in Fig. 3. The three g-values correspond to three orientations of the magnetic field with respect to the CO_2^-

radical: (1) for g_z the magnetic field is parallel to the symmetry axis of the ion, (2) for g_x the magnetic field is perpendicular to the symmetry axis and to the CO_2^- plane, and (3) for g_y the magnetic field is perpendicular to the symmetry axis and parallel to the CO_2^- plane. The three different g-values support the concept of a bent structure for the radical ion rather than a linear structure. Overall and Whiffen use the C^{13} coupling constants to show that the unpaired electron in CO_2^- is primarily in a pseudo π-antibonding orbital that projects along the external bisector of the O C O angle. The magnitude of the coupling constants for the CO_2^- radical ion on MgO is somewhat greater than for CO_2^- in Na COOH, but the degree of anisotropy is about the same. This indicates that the Fermi contact term, a measure of the **s**-character of the molecular orbital, is slightly larger for the radical ion on MgO. Overall and Whiffen further show that the O C O angle is 134° in agreement with the O N O angle in NO_2, which is an iso-electronic molecule with the CO_2^- radical.

The EPR spectrum of carbon dioxide on unirradiated MgO shows no CO_2^- radical ions. Magnesium oxide is a good electrical insulator, which means that there exists a wide forbidden region and there are no filled electron or hole traps near the conduction or valence band. The ultraviolet light provides energy for exciting electrons to these intrinsic defects on the surface where the energy is stored as a trapped electron. The adsorption of a CO_2 molecule by a charge transfer offers than a path for some of this stored energy to be released. It will be interesting to see if such radical ions can be detected on the surface of metals where the work function is much lower.

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TABLE I. - TABLE OF g-VALUES

	g_z	g_x	g_y	Estimated error
CO_2 on MgO	2.0017	2.0029	1.9974	±0.0003
CO_2^- in γ-irradiated NaCOOH (ref. 7)	2.0014	2.0032	1.9975	±0.0002
S' center	2.0005	2.0015	1.9990	±0.0003
S center (ref. 5)	[a]2.0007	------	------	±0.0002
F_2 center (ref. 8)	2.0008	------	------	±0.0002

[a]Only one apparent g-value was reported for these centers since the anisotropy is of the same magnitude as the line width.

TABLE II. - HYPERFINE COUPLING CONSTANTS

	Hyperfine coupling constants, gauss		
	A_z	A_x	A_y
CO_2 on MgO	230	[a]184	---
CO_2^- in NaCOOH (ref. 7)	195	156	151

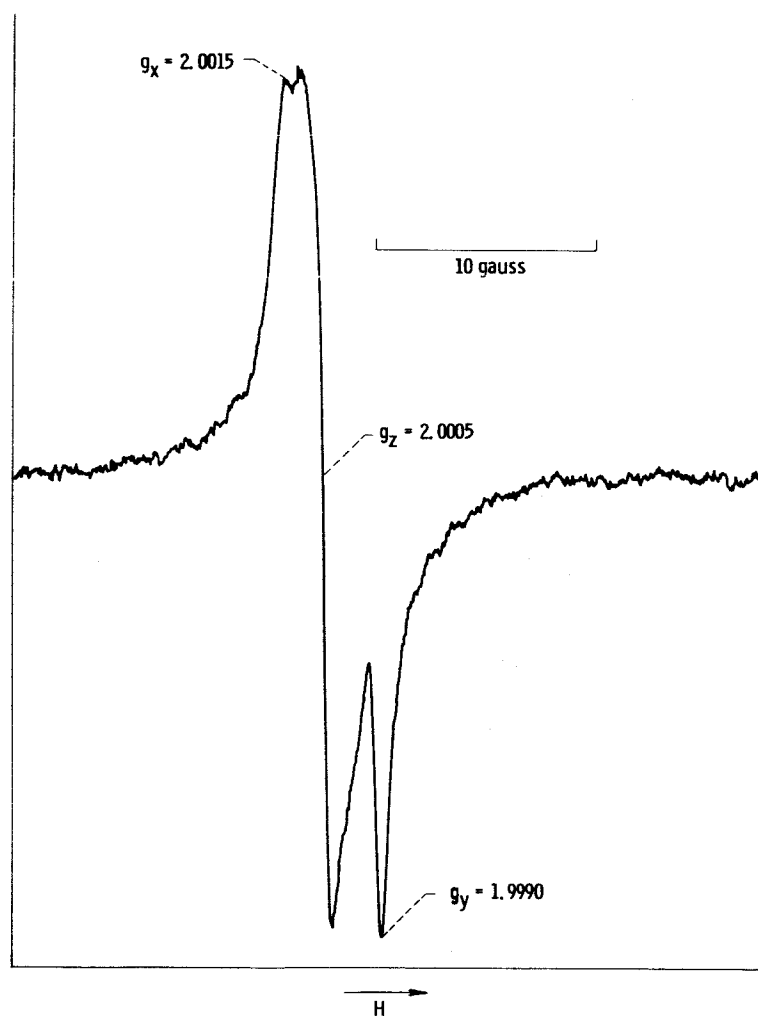[a]In the powder samples it was not possible to resolve A_x and A_y.

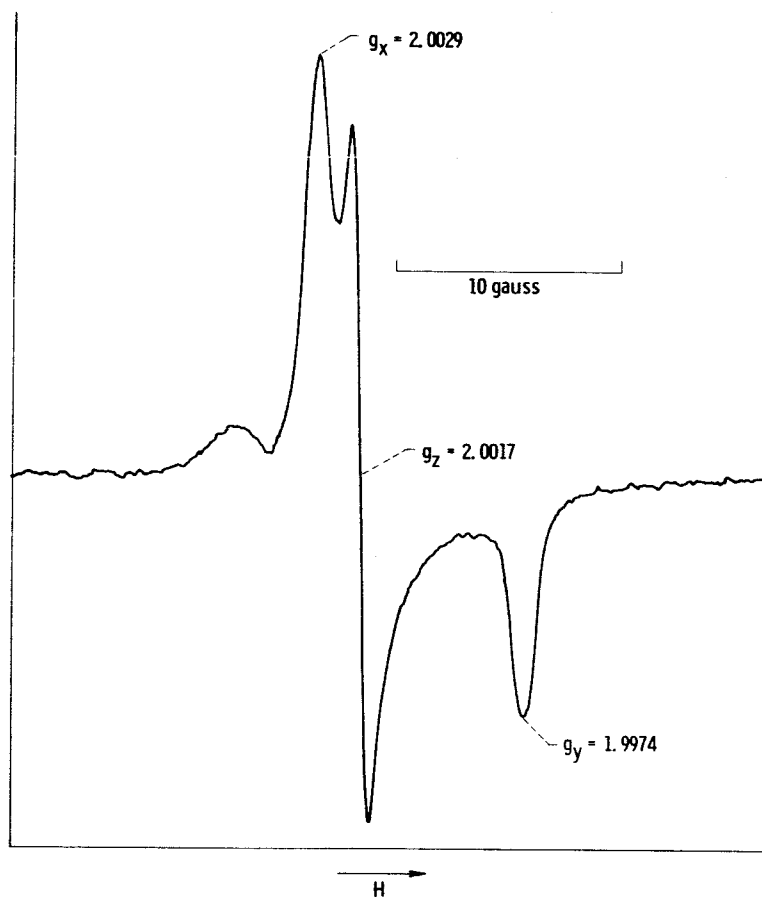Figure 1. - S' spectrum of ultraviolet irradiated magnesium oxide.

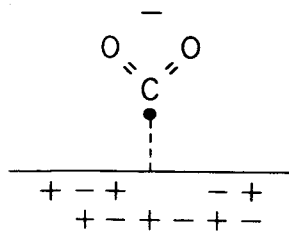Figure 2. - EPR spectrum of carbon dioxide adsorbed on ultraviolet irradiated magnesium oxide.

Figure 3. - Model for CO_2^- formation on irradiated magnesium oxide from EPR data.