

LETTERS

N₂⁻ Radical Anion Reversibly Formed at the Surface of “Electron-Rich” Alkaline-Earth Oxides

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Physisorption of N₂ gas onto the surface of a metal oxide (MgO or CaO), containing paramagnetic trapped electron centers (F_s⁺ color centers), leads to the formation of a paramagnetic species that, on the basis of its EPR spectrum and of the related spin-Hamiltonian parameters, is identified as a N₂⁻ radical anion. The species in fact contains two nitrogen atoms and its **g** and **A** tensors are in agreement with what observed for the N₂⁻ radical trapped in irradiated crystal of various azides. The surface N₂⁻ species is formed by surface-to-molecule one-electron transfer, and its stability strictly parallels the stability of the physisorbed layer, the species formation being completely reversible and pressure dependent. When the N₂ adlayer is desorbed, in fact, the N₂⁻ spectrum vanishes and the original F_s⁺ spectrum is restored. Ab initio quantum chemical calculations on an embedded MgO cluster fully confirm the observed phenomenon indicating, in agreement with EPR analysis, the electron transfer of a large fraction of electron density into the π orbitals of the ad molecule.

Introduction

In the title of a recent paper by Gutsev et al.,¹ the question about the existence of the N₂⁻ radical anion was postulated and both the stability and decay of this anion to the neutral parent molecule plus a free electron were discussed on the basis of

sophisticated quantum chemistry calculations. Most of the experimental work on such radicals and other negative species are based on the interaction of target molecules with incident electrons, and the resulting short-lived species are called *resonances* or *temporary negative ions*.² In the present Letter,

we present evidence for the first observation of the N_2^- radical anion adsorbed on a oxide surface, which is *formed directly by nitrogen adsorption*. The anion is stable, although in a limited range of temperatures and N_2 pressure, and is formed by adsorption of nitrogen onto MgO (and CaO) containing surface trapped electrons or $F_S^+(H)$ centers. The entire process of N_2^- formation was also simulated by quantum chemistry calculations which fully confirm and support the experimental data.

Results and Discussion

The surface-trapped electron centers can be formed on the alkali-earth oxides by different methods including exposure of the activated oxide to high-energy radiation³ or addition of metal vapors.^{4,5} In all cases, "electron-rich surfaces" are obtained which contain both pairs of trapped electrons (producing F_S centers; effectively neutral) and single unpaired electrons (called F_S^+ centers which are paramagnetic) in suitable surface oxygen vacancies. These trapped electron centers are the surface equivalent (hence the subscript "s") of the more familiar bulk color centers or F centers common in ionic oxides and halides. In the particular case of $F_S^+(H)$ centers,^{6,7} the electron-rich surface is generated by UV irradiation of MgO or CaO containing preadsorbed hydrogen. Heterolytic chemisorption of hydrogen occurs on the activated surface⁸ forming H^+ and hydride H^- ions, the latter being subsequently ionized by the UV irradiation. The electron released from the hydride is stabilized at a surface oxygen vacancy close to the OH^- formed by reaction of H^+ with a surface O^{2-} ion.^{6,7} Nevertheless, from the chemical reactivity viewpoint, both F_S^+ and $F_S^+(H)$ centers are equivalent.

High surface area polycrystalline MgO and CaO samples were prepared by decomposition of the corresponding magnesium hydroxide and calcium carbonate under vacuum. This produces polycrystalline oxides with a high surface area ($\approx 200 \text{ m}^2 \text{ g}^{-1}$ for MgO, $\approx 75 \text{ m}^2 \text{ g}^{-1}$ for CaO). Precise details on the generation of the $F_S^+(H)$ color centers are reported elsewhere^{6,7} and basically involve UV irradiation of the activated oxide in equilibrium with 100 Torr of hydrogen at about 100 K. The resulting colored solid exhibits an axial EPR spectrum with $g_{\parallel} = 2.000$ and $g_{\perp} = 1.999$ at X-band frequencies (9 GHz) and a characteristic hyperfine coupling (of about 2 G for MgO and 4 G for CaO) in the perpendicular direction due to interaction of the unpaired electron with the 1H of the nearby OH group.⁶⁻⁸

Figure 1 shows the powder EPR spectrum of the $F_S^+(H)$ centers on MgO (Figure 1a) and the effect on the spectrum after adsorption of 100 Torr of N_2 at 77 K (Figure 1b). Under such conditions, the nitrogen gas is physisorbed on the surface with a coverage of just greater than one monolayer. It can be clearly seen that the structure of the original spectrum (Figure 1a) is dramatically changed upon N_2 adsorption, and shows a complex but well-resolved powder spectrum characterized by a high number of lines (Figure 1b). However, formation of the new signal (Figure 1b) by N_2 adsorption is *completely reversible*; removal of the physisorbed N_2 by either evacuation or increasing the temperature immediately restores the original $F_S^+(H)$ signal (Figure 1a). On reducing the coverage of adsorbed nitrogen, either by reducing the equilibrium pressure or by raising the temperature, a mixed spectrum (a sort of superimposition of spectra a and b) can be observed. Although in these mixed spectra the features of the new signal are, due to the reduced intensity or to the higher temperature, less defined than in Figure 1b, there is matter enough to suggest that the observed phenomenon is pressure dependent and totally reversible in tandem with the trend of N_2 physisorption on the surface.

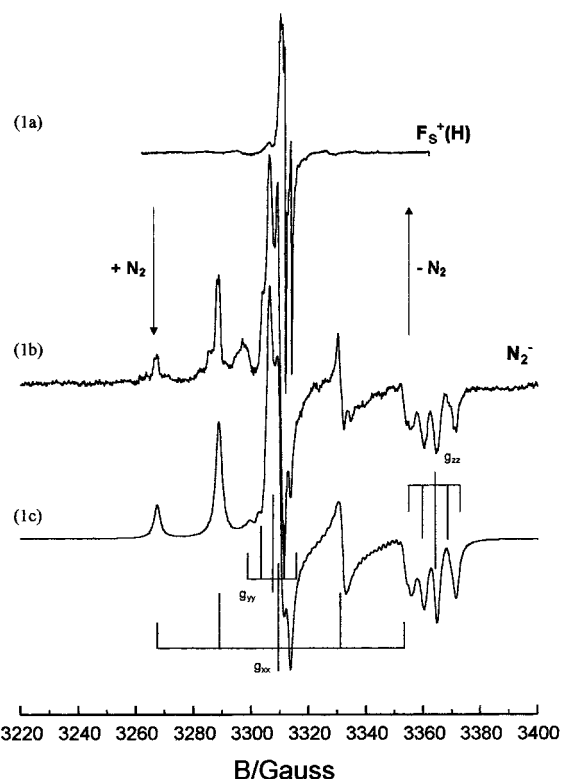


Figure 1. (a) EPR spectrum of the $F_S^+(H)$ center on the MgO surface under vacuo (10^{-5} Torr), and (b) spectrum of the N_2^- radical anion after adsorption of N_2 (60 Torr) at 77 K. The computer simulation of the N_2^- spectrum is shown in (c). All spectra were measured at 77 K.

TABLE 1: Spin Hamiltonian Parameters for the $^{14}N_2^-$ Radical Anion Adsorbed on MgO and in Various Solid Matrices

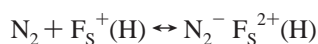
	spin Hamiltonian parameters for N_2^- in several hosts					
	g_{xx}	g_{yy}	g_{zz}	A_{xx} (G)	A_{yy} (G)	A_{zz} (G)
N_2^- on MgO (this work)	2.0042	2.0018	1.9719	21.5	2.9	4.2
N_2^- in KN_3 (ref 9)	2.0027	2.0008	1.9832	12.0	3.8	4.0
N_2^- in NaN_3 (ref 10)	≈ 2.00	≈ 2.00	1.75	23.5	11.0	3.9
N_2^- in $Ba(N_3)_2$ (ref 11)	≈ 1.99	≈ 1.99	1.979	20.7	3.6	4.1

The computer simulation of the new spectrum (Figure 1c) was obtained using the spin-Hamiltonian parameters listed in Table 1 and based upon an $S = 1/2$ species with anisotropic \mathbf{g} and \mathbf{A} tensors. In particular, the hyperfine structure of this species was simulated on the assumption of two nearly equivalent N atoms. For solution or single-crystal EPR spectra, this situation would produce a spectrum with a quintuplet of lines having the intensity ratio 1:2:3:2:1 ($I = 1$ for ^{14}N). However, the shape of a powder EPR spectrum with rhombic character will be far more complicated and can only be confidently assigned after a satisfactory computer simulation (Figure 1c).

The \mathbf{g} tensor of the new species (Table 1) is in complete agreement with that expected for an 11-electron N_2^- radical anion. Previous examples in the literature on stable N_2^- radicals were only observed in the bulk of irradiated single crystals of metal azides⁹⁻¹¹ but the reported spin-Hamiltonian parameters are in excellent agreement with our data (Table 1). The observed \mathbf{g} tensor has two elements close to the free electron g value ($g_e = 2.0023$) and a third one at $g < g_e$ as predicted for π diatomic radicals with one electron in the π^* antibonding orbitals¹² and observed for other surface-adsorbed 11-electron radicals like NO^{13} and CO^- .¹⁴ In particular, the low value of the third \mathbf{g}

component (i.e., parallel orientation to the internuclear axis) is a characteristic feature or fingerprint for these types of radicals.

On the basis of the *g* and hyperfine tensors, the latter indicating the presence of two practically equivalent nitrogen atoms, the observed species can be confidently assigned to an N_2^- radical anion formed by physical adsorption of the nitrogen molecule onto an oxide surface containing electrons trapped at the surface vacancies. The anisotropy of both *g* and *A* tensor indicates that, at 77 K, the motion of the species is not enough fast to cause remarkable averaging of the tensor elements. The same situation was found for the $^{17}\text{O}_2^-$ radical formed by interaction with F_s^+ centers on MgO .¹⁵ The magnetic equivalence of the two N nuclei (Table 1) also suggests that the anion lies parallel to the surface. Remarkably, the process is totally reversible and, once the adsorbed nitrogen layer is removed, neutral N_2 molecules are desorbed while the unpaired electron is transferred back into the surface trap. The equilibrium process can be represented as follows:



where $\text{F}_\text{s}^+(\text{H})$ represents the vacancy containing one unpaired electron and $\text{F}_\text{s}^{2+}(\text{H})$ the empty oxygen vacancy. A thorough analysis of the N_2^- spin-Hamiltonian parameters and the spectral behavior as a function of temperature will be reported in a forthcoming paper. However, a preliminary analysis of the hyperfine constants indicates that the unpaired electron density on each N is ≈ 0.385 with a negligible contribution from the 2s atomic orbital and a substantial contribution from the two π^* antibonding orbitals. Again, this distribution is in agreement with the expected *g* values of an 11-electron radical with $^2\Pi_\text{g}$ ground state. In other words, about 77% of the spin density is transferred to the incoming nitrogen molecule upon adsorption. We have also observed similar spectra, though slightly less resolved, following N_2 adsorption on surface F_s^+ centers (i.e., no neighboring OH group) generated on MgO either by exposure of the oxide to metal vapors or alternatively by X-ray irradiation of the solid. Further confirmation for the N_2^- assignment comes from spectra (not reported here) recorded using $^{15}\text{N}_2$ which reveal the expected changes from an $I = 1$ nucleus of ^{14}N to an $I = 1/2$ nucleus of ^{15}N . A spectrum somewhat similar to that shown in Figure 1b was previously reported by some of us¹⁶ and incorrectly assigned due to its strong similarity with spectra obtained by methane adsorption on the same surface. This will be discussed in a forthcoming publication.

A theoretical investigation of the current system was also attempted using ab initio quantum chemistry methods. An $\text{O}_{12}\text{-Mg}_{13}$ cluster embedded in effective core potentials and within a large set of point charges^{17,18} was used to simulate an oxygen vacancy at the MgO surface with a trapped unpaired electron (F_s^+) and its resulting interaction with a N_2 molecule. Potential energy curves have been determined at the Hartree–Fock (HF) level as a function of the distance *r* of N_2 from the surface plane using double- ζ plus polarization quality basis sets (Figure 2) (for further details see also refs 17 and 18). The first curve is related to the $\text{F}_\text{s}^+/\text{N}_2$ system and is purely repulsive indicating that a very weak interaction should be expected between neutral N_2 and the F_s^+ center. Of course, dispersion forces cannot be described at the HF level and the physisorbed state is not properly represented. When the N_2 molecule approaches the surface the electron transfer is favored and a second doublet state, dissociating into F_s^{2+} and N_2^- , becomes lower in energy, in agreement with the experimental results. The results have been checked by performing more accurate calculations at the density functional theory level, using more flexible basis sets

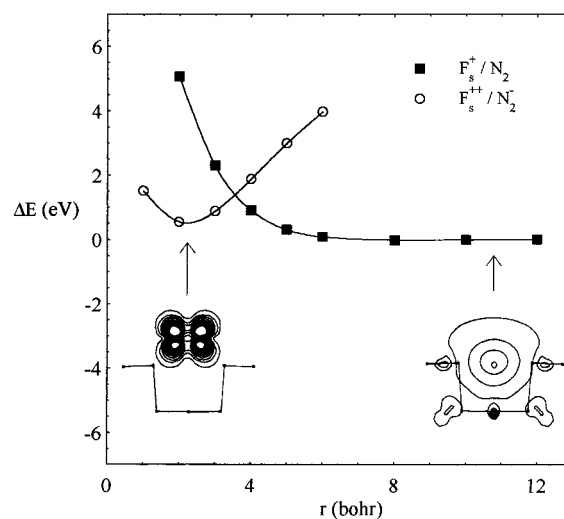


Figure 2. Hartree–Fock potential energy curves for the interaction of N_2 with an F_s^+ center at the surface of MgO (■—■). The figure shows that at short distances, the state corresponding to $\text{F}_\text{s}^{2+}/\text{N}_2^-$ becomes lower in energy (○—○). Isocontour lines of the spin density show the different localization of the unpaired electron for large and short N_2 – MgO distances. The contour lines are drawn in a plane normal to the MgO surface containing the N_2 molecule with intervals of 0.005 e/au^3 .

on N_2 in order to properly describe its electron affinity and with inclusion of surface relaxation: the $\text{F}_\text{s}^{2+}/\text{N}_2^-$ complex is almost isoenergetic with the $\text{F}_\text{s}^+/\text{N}_2$ dissociation limit.¹⁹ The reason for the stability of the charge transfer state is due to the strong electrostatic attraction between F_s^{2+} and N_2^- .^{17,18} The isocontour lines of the spin density (Figure 2) for two particular surface– N_2 distances show effectively the electron transfer process taking place at the surface. A crude estimate of the activation energy for desorption from the intersection of the two curves in Figure 2 shows that this is not large, consistent with the observed easy desorption of nitrogen in its neutral molecular form. More accurate calculations with inclusion of correlation effects and full geometry optimization are in progress in order to better describe the height of the barrier as well as the hyperfine constants of adsorbed N_2^- . Nevertheless, these preliminary theoretical results are in full agreement with the described experimental observations.

In conclusion, we note the following: (a) this is the first experimental observation of a surface stabilized N_2^- radical anion and the EPR spectrum (Figure 1b) is, moreover, the first powder spectrum ever reported for such species; (b) in comparison to the short-lived temporary negative ions,² the present N_2^- anion is completely stable at 77 K due to the stabilizing effect of the ionic surface and furthermore is stable in a wide range of temperatures corresponding to the temperature dependence of N_2 physisorption; (c) the observed interaction between nitrogen and the electron-rich surface shows the remarkable property of a surface-to-molecule one-electron transfer process, involving almost the entire electron density, but at the same time is totally reversible.

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