Evidence for Ammonia Solvated Electrons Stabilized at the Surface of Magnesium Oxide.

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Abstract. We report on the magnetic properties of solvated electrons localized at the surface of magnesium oxide and obtained by reaction of ammonia with surface excess electrons. Excess electrons can be stabilized at the surface of insulating ionic oxides by strong local potentials of positive and negative ions in particular arrays and in some circumstances by single cations. Exposure of these centres to NH3 leads to ammoniated electrons analogous to those obtained by dissolution of alkali metals in liquid ammonia.

1. Introduction.
Solvated electrons are remarkable chemical entities which provide great potential for understanding reaction mechanisms in chemistry and biology as well as in the synthesis of new solid state compounds with precisely tuned electronic and magnetic properties.[1-3] This is also true when excess electron localisation is confined to the surface of solid materials.[4] In this case due to the complex morphology and defectivity of real surfaces, the localisation of excess electrons represents a challenging problem and a promising area of research for both experimentalists and theoreticians. [5-7] Due to their potential role in affecting properties such as charge injection and transport at interfaces, solvated electrons are becoming an important topic among surface scientists.

Since more than one decade our group is engaged in the study of the surface properties of alkaline-earth oxides in terms of structure, morphology, defectivity and reactivity. [8-10] These oxides exhibit high ionicity, simple structure (NaCl) and a relatively well defined morphology based on highly extended (100) planar faces. Some of these oxides, in particular MgO, can be prepared in polycrystalline form with different morphology and surface area. MgO smokes or synthered samples exhibit very low concentrations of low-coordinated sites and morphological defects while high surface area samples derived from the corresponding hydroxide exhibit a non negligible fraction of surface irregularities (steps, kinks, edges, corners etc.). It is at these very sites that excess electron trapping can occur leading to “electron-rich” surfaces. In particular H atoms spontaneously dissociate at low coordinated MgO pairs to give (H+)(e-) pairs stabilized at the surface, which are responsible for the blue colour acquired by the MgO powder. These surface excess electron centres offer unexplored opportunities to tune the electronic and magnetic properties of the solid and give rise to a specific chemical reactivity.

Particularly intriguing is the reactivity of surface excess electron centres on MgO with ammonia, which we report on in the following. The reaction leads to resolved EPR spectra characterized by 14N hyperfine coupling to three equivalent N atoms and a broad absorption band in the near infrared region.
centered at about 0.75 eV. These properties are those expected for ammonia solvated electrons stabilized at the oxide surface, analogous to solvated electrons formed by dissolution of alkali metal atoms in liquid ammonia.

2. Experimental section.
High surface area MgO (200 m$^2$g$^{-1}$) was obtained by slow thermal decomposition under dynamic vacuum of the corresponding hydroxide (Aldrich). The oxide was then activated at 1173K for 1 h. The hydrogen atoms were produced in a 2.45 GHz microwave discharge under static conditions. Typical hydrogen pressure was 0.3 mbar.

EPR spectra were recorded on a Bruker EMX spectrometer operating at X-band frequencies and equipped with a cylindrical cavity operating at a 100 KHz field modulation. The spectra have been recorded at 1 mW microwave power. The sample was cooled by a gas-flow cryostat operated from T=4.0 K to 300 K. DPPH (g=2.0036) and a solid solution of Mn$^{2+}$ in MgO (g=2.0064) have been used as standards for g-value calibration.

The EPR computer simulations were performed using the EPRSIM32 program developed by Prof. Z. Sojka (Jagiellonian University, Cracow). [11]

UV-VIS-NIR (Varian Cary-5) spectra were recorded in situ on the same sample employed for the EPR analysis using a quartz cell equipped with both a cell for optical measurements and an EPR tube.

3. Results and discussion.
Atomic hydrogen undergoes spontaneous ionization over surface morphological features of MgO leading to surface excess electron-proton pairs stabilized at low co-ordinated Mg$^{2+}$-O$^{2-}$ ions. The so formed (H$^+$)(e$^-$) centres have an optical spectrum characterized by a distinct absorption pattern (figure 1a), dominated by two absorption bands with maximum at 1250 nm and 730 nm. Annealing experiments show that these absorption features are correlated to the EPR spectrum shown in figure 1b.

![Figure 1.](image-url) a) UV-Vis-NIR spectrum of (H$^+$)(e$^-$) centres at the surface of MgO; b) EPR spectrum of (H$^+$)(e$^-$) centres at the surface of MgO; c) UV-Vis-NIR spectrum recorded after reaction with 1 mbar of NH$_3$; d) EPR spectrum of c). Arrows in the UV-Vis-NIR spectra indicate artefacts due to spectrometer background.
The EPR spectrum of (H\(^+\))(e\(^-\)) centres (figure 1b) is dominated by an axial feature with \(g_{\|} = 1.999\) and \(g_{\perp} = 2.001\) and is primarily characterized by a resolved doublet hyperfine splitting of about 2 G. This splitting arises from the magnetic interaction between the unpaired electron and the H nucleus of a neighboring OH\(^-\) group and has been thoroughly discussed elsewhere. [12]

![Figure 2. a) EPR spectrum recorded after reaction of (H\(^+\))(e\(^-\)) centres with 1 mbar of \(^{14}\)NH\(_3\); b) spectrum recorded after reaction with \(^{15}\)NH\(_3\).](image)

When ammonia (0.8 mbar) is contacted with the electron rich MgO sample, a colour change is observed which results from a marked in the absorption spectrum (figure 1c). The Uv-Vis-NIR variation spectrum after ammonia adsorption is in fact dominated by a broad and pronounced band centred at about 1650 nm (0.74 eV), while the feature at 730 nm is red shifted to 940 nm. The modifications in the absorption spectrum is accompanied by a dramatic change in the EPR spectrum (figure 1d).

The new spectrum is characterized by 7 equally spaced lines with average separation of about 11 G and relative line amplitudes 1:3:6:7:6:3:1. This result can be interpreted in terms of the interaction of the unpaired electron with three equivalent \(^{14}\)N nuclei (\(I = 1\)) and this analysis is confirmed by experiments performed with \(^{15}\)NH\(_3\) (\(^{15}\)N \(I = 1/2\)). The spectrum observed upon interaction of (H\(^+\))(e\(^-\)) centres with \(^{15}\)NH\(_3\), shown in figure 2b, is characterized by 4 lines with intensity ratio 1:3:3:1 and hyperfine separation scaled by the ratio between \(^{15}\)N and \(^{14}\)N magnetic moments, confirming that the main source of hyperfine interaction arises from N nuclei. The spin Hamiltonian parameters were extracted by means of computer simulation of the spectrum (figure 3), the best fit of the experimental spectrum was obtained with isotropic \(g\) and \(A\) tensors with values \(g_{av} = 2.0010\) and \(a = 11.0 \pm 0.5\) G.

No hyperfine proton coupling was detectable in the CW spectra and experiments performed with ND\(_3\) did not lead to appreciable variations in the line width indicating that the proton hyperfine interaction is indeed too small to detect.

The main features of the results are thus as follows.

(i) The interaction of ammonia with surface (H\(^+\))(e\(^-\)) centres lead to a dramatic change in both the EPR and electronic absorption spectrum of the sample. In particular the onset of the septet EPR spectrum observed for \(^{14}\)N ammonia, indicating that the unpaired electron
interacts with three equivalent $^{14}$N nuclei, is accompanied by a broad absorption band centred at about 0.75 eV.

(ii) Experiments performed with deuterated ammonia demonstrated that the proton hyperfine interaction is too small to detect under the experimental conditions.

(iii) The $g$ value of the signal is lower than the free electron value ($g_e = 2.0023$). Anisotropy, if any, is small and buried within the line-width of the signal.

These results can be explained by considering that the centres formed upon adsorption of ammonia on surface excess electron centres on MgO, closely resemble the solvated electron centres formed when alkali metals dissolve in liquid ammonia, a suggestion first made by Symons. [13]

![Figure 3. Experimental (a) and computer simulated (b) EPR spectra of ammoniated electrons on MgO.](image)

Strong evidence for this is brought by the absorption spectrum (Fig. 1c) which is strikingly similar to what observed for alkali metal atoms in liquid ammonia. In a similar way the $^{14}$N hyperfine coupling is close to expectation for the primary solvation shell in metal ammonia solutions. It should be stressed that this coupling has never been observed experimentally in fluid solution due to exchange narrowing of the spectra, while in frozen solutions only broad lines with no resolved features have been reported [14]. However the Nitrogen-14 Knight shift in metal ammonia solutions has been measured accurately [15]. This yields the unpaired electron spin density over all the nuclei comprised within the unpaired electron orbit. In other words the total electron spin density on $n$ equivalent solvent nuclei, constituting the strong interacting primary shell and weakly interacting secondary and third shells is measured. This gives a total nitrogen isotropic coupling of ca. 110 G for sodium ammonia solutions consistent with $^{14}$N coupling of ca. 12 G for each of six solvent molecules in the first solvation shell. This result is totally consistent with the value reported above for the MgO surface stabilized species.

The crucial question arises then on the precise nature of the orbitals where the unpaired electron is allocated. The classical model for the solvated electron is based on a idealized particle-in-a-box approach, where the unpaired electron resides in the cavity made by the solvent, a model which easily accounts for the broad absorption ($s \rightarrow p$) band in the near-infrared (IR). This cavity model, which was first suggested by Ogg [16] and later developed by Jortner, [17] forms the basis of many theoretical computations. These show the cavity to be formed by Pauli repulsion of the excess
electron by the valence ammonia electrons, leading to volumes corresponding to a sphere of about 3 Å. According to this model, analogous to that of the \( F \) centres in ionic solids, the majority of the excess electron density is contained within the cavity and transfer of spin density to the frontier orbitals of nitrogen atoms constituting the cavity walls is expected to be small. This seems to be consistent with the results reported above. In particular, considering that the hyperfine coupling expected for unit occupancy of the 2s nitrogen orbital is estimated to be ca. 600 G [18], the total unpaired electron spin density spread over the three nitrogen nuclei will be of about 5%. This standard analysis of spin repartition is however full of risk as recently shown by some of us in the case of alkali metal atoms adsorbed on MgO. [19] In particular the assumption that it is the 2s N orbital that contributes to the actual molecular orbital is a pure guess. In order to fully explain our results, in fact, a group orbital is required which encompasses three ammonia molecules. This orbital must have almost no p character and a node close to the hydrogen atoms. A combination of suitably modified 3s orbitals on nitrogen may represent a sound and to the point choice. Interestingly the first excited state orbital on ammonia is a Rydberg-like level constructed with 3s N atomic orbitals and recent ab-initio calculations [20] on the Rydberg molecule \( \text{NH}_4 \) have shown that the unpaired electron is indeed allocated in a N 3s orbital and the calculated hyperfine coupling constant to the N nucleus is found to be of the order of 70 G, while coupling to the protons is negligible. Interestingly the EPR spectrum of Li-\( \text{NH}_3 \) units isolated in rare-gas show absence of anisotropy, no proton coupling and nitrogen hyperfine coupling of the order of 15 G [21]. The hyperfine coupling constant for an electron in an orbital resembling the N 3s level may thus be expected to range between 20 to 70 G. If we consider this option then the unpaired electron will be largely accounted for by the summation over the N 3s orbitals, without need to invoke high electron density elsewhere. In this way the surface stabilized “ammoniated electron” can be accounted for by a multimer radical anion in which most of the electron density is allocated into the frontier orbitals of N atoms of the ammonia molecules forming the solvation cavity, a suggestion first made by Symons [13] and recently reconsidered on the basis of DFT calculations for ammonia cluster anions. [22]

![Figure 4. Proposed model for ammonia solvated electrons on MgO.](image-url)

Whether this picture holds in the case of surface stabilized solvated electrons on MgO remains uncertain in particular considering the further complication introduced by the interaction of ammonia with the MgO surface. The adsorption of ammonia on MgO has been thoroughly studied [23,24] and it was shown by means of I.R. experiments that \( \text{NH}_3 \) is adsorbed both molecularly and dissociatively on
MgO powders thoroughly dehydrated. In particular a small fraction (10%) of ammonia undergoes heterolytic dissociation on cation-anion couples to form $\text{NH}_3^-$ and $\text{H}^+$ groups. The surface sites involved in this dissociative adsorption are also the sites responsible for electron trapping. Thus the possibility that the solvating cage is made by $\text{NH}_3^-$ fragments should be considered.

A final crucial question concerns the exact structure and localization of these centres on the MgO surface. The EPR spectra show unambiguously that the excess electron interacts with three equivalent nitrogen nuclei. Given the NaCl like structure of MgO, a possible site bearing the correct symmetry requirements, may be a oxygen terminated corner site as the one shown in Figure 4, where the unpaired electron is confined within three magnetically equivalent $\text{NH}_3^-$ ions formed by ammonia dissociation on the three edges.

This tentative model should however be tested against theoretical modelling. We believe that these experimental data, in combination with ab-initio calculations may allow, not only to understand the structure of solvated electrons stabilized at the MgO surface, but also to shed light on the general and vexing problem of the microscopic nature of solvated electrons in ammonia.

4. Conclusions.
Reaction of ammonia with (H$^+$(e$^-$) centres on MgO lead to surface excess electron centres that closely resamble solvated electrons in liquid ammonia. The new centres are characterised by a broad absorption in the near I.R. and by EPR spectra with resolved N hyperfine interaction. In particular the unpaired electron interacts with three equivalent nitrogen nuclei, while no proton coupling is observed. A tentative model for these centres is proposed and the possibility that the excess electron is allocated in the frontier orbitals of surface $\text{NH}_3^-$ groups is advanced.

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