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Photo-oxidation of sulfite ions in the presence of some iron oxides

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Abstract

The photocatalytic oxidation of sulfite ions over different iron oxides samples is investigated. For the different hematite samples tested, the experimental data of sulfite photo-oxidized vs. irradiation time can be adjusted fairly well to a kinetic equation of the type $dx/dt = K(1-x)/x$, where x is the fraction of sulfite reacted at time t. The behaviour described by this equation corresponds to an heterogeneous process where the product of reaction is strongly adsorbed on the substrate. The rate constant K obtained for the different hematite samples can be related to their respective specific surface area. Fe(II) species were detected in solution when hematite suspensions were irradiated. These Fe(II) ions are assumed to be formed through photoreduction of lattice Fe(III). On the contrary, for magnetite and maghemite suspensions no Fe(II) ions were detected in solution after irradiation. In the latter case, crystalline phase transformation is assumed to take place.

Keywords: Photo-oxidation; Sulfite ions; Iron oxides

1. Introduction

Iron oxides are common materials that have the ability to photocatalyze some chemical reactions [1–7]. In those photocatalytic processes, the semiconductor particles, upon absorption of light of suitable energy, generate electron-hole pairs which after migration to the semiconductor–electrolyte interface react with redox species in solution [8]. The bandgap of the different natural iron oxides lies around 2 eV [3], which points to the possibility of solar irradiation photoactivation of these semiconductor materials. Consequently, the iron oxides, which are common constituents of many natural environments, could play a non-negligible role in biogeochemical cycles. Since the oxidation of SO_2 by solid particles suspended in atmospheric water droplets seems to be a viable reaction pathway for the formation of acid rain [9], we have chosen sulfite as model compound in order to investigate the photocatalytic activity of different iron oxide samples. Particularly, we focus our attention in the study of the photocatalytic activity of some samples of hematite, magnetite and maghemite, which are commonly present in different natural environments.

2. Materials and methods

All chemicals used were, at least, of reagent grade. Sodium sulfite (Merck) was used as sulfite source. Hematite, magnetite and maghemite were chosen as solid iron oxides phases. Three samples of α-Fe_2O_3 were used: (i) hematite A, synthesized by hydrolysis at high temperature (95 °C) of solutions of 0.02 M $FeCl_3$ and 0.0016 M HCl, in a vertical reactor with continuous flow (residence time 24 h), in a similar way to what has been described elsewhere [10]; (ii) hematite B, prepared by hydrolysis of a solution of 0.02 M $FeCl_3$ and 0.0016 M HCl in an oven at 100 °C, for 24 hours, following the method described by Matijevic [11]; hematite C was prepared in a similar way, but the concentration of HCl employed was 0.001 M. Magnetite was obtained by precipitative oxidation and it was used as the starting material for the obtention of maghemite

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The low-lying excited states of 1,6-methano[10]annulene

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Abstract

The electronic absorption spectrum of 1,6-methano[10]annulene in the region of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions was investigated at room and low temperature. By comparison with the one-photon spectrum of naphthalene, and considering pseudoparity selection rules, the strong 33 000 cm^{-1} band of the annulene derivative is assigned as the inductively perturbed $S_0 \rightarrow S_2$ (L_a^+) electronic transition. The rich vibronic structure of the $S_0 \rightarrow S_1$ transition at low temperature is discussed in terms of Franck–Condon allowed transitions. The calculated intensities of the fundamental modes are in qualitative agreement with the experimental data. © 1997 Elsevier Science S.A.

Keywords: Electronic absorption spectra; Low-lying excited states; 1,6-Methano[10]annulene

1. Introduction

Aromaticity is a powerful guideline to the understanding of the properties of conjugated cyclic π-electron systems [1,2]. In the case of annulenes, i.e. the higher homologues of benzene with $(4n+2)$ π electrons, distortion from planarity may decrease the π delocalization and isomerism may occur as a result of the structural flexibility [3]. However, it is generally established [2] that a more rigid σ framework, as supplied by bridgehead links between opposite C atoms or by the formation of triple bonds along the chain, favours the aromatic stabilization of the bond-equalized geometry over the cyclopolyenic arrangement of alternating single and double bonds.

There are good indications that the spectroscopy of bridged [10]-, [14]- and [18]-annulenes conforms to the aromatic behaviour. The subject has been thoroughly discussed in earlier studies [4–6]. In this paper, we address the pseudoparity properties [7] of excited molecular wavefunctions in bridged 1,6-methano[10]annulene (see Fig. 1), due to the nature of alternant hydrocarbon, and the relation with the observed UV spectrum. Pseudoparity selection rules have been used for electronic assignment in simple aromatics [8–10] and may be particularly suitable in the discussion of low-energy transitions of annulenes which remain unclear [6].

Apart from assignment, the excited states of bridged annulenes have not received much attention so far. Their degree of aromaticity or, in other words, to what extent the excitation to virtual molecular orbitals (MOs) changes the cyclic structural arrangement is an important piece of spectroscopic information in its own right as well as in relation to intramolecular photoprocesses. The analysis of the $S_0 \rightarrow S_n$ absorption profiles may provide important clues on this point. If the electronic transition is allowed, the Franck–Condon envelope of vibronic transitions depends, among other things, on the position of the excited state potential well with respect to the ground state [11–13]. To this end, we have measured the $S_0 \rightarrow S_1$ absorption spectrum of 1,6-methano[10]-annulene at low temperature. The intensity profile of the vibronic bands indicates that, on excitation, a geometry change occurs towards a more delocalized structure.

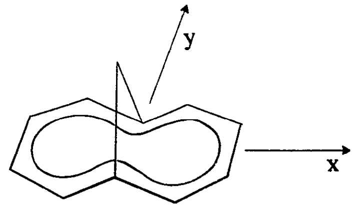

Fig. 1. Molecular structure of 1,6-methano[10]annulene.

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$$(Fe^{3+}-O^{2-}-Fe^{3+}(OH^{\cdot}))+SO_3{}^{2-}{}_{ads} \longrightarrow (Fe^{3+}-O^{2-}-Fe^{3+}(OH^{-}))+SO_3{}^{\cdot -}{}_{ads} \quad (8)$$

The photogenerated conduction band electrons are highly energetic, thus reducing the adsorbed oxygen on the semiconductor and/or reducing the lattice Fe(III). This last process leads to the photocorrosion of the Fe_2O_3 [16]:

$$(Fe^{3+}-O^{2-}-Fe^{3+})+e^{-} \longrightarrow (Fe^{3+}-O^{2-}-Fe^{2+}) \quad (9)$$

$$(Fe^{3+}-O^{2-}-Fe^{3+}(O_2)_{ads})+e^{-} \longrightarrow (Fe^{3+}-O^{2-}-Fe^{3+}(O_2{}^{-})_{ads}) \quad (10)$$

$$(Fe^{3+}-O^{2-}-Fe^{2+}) \longrightarrow Fe^{2+}{}_{sol} \quad (11)$$

In fact, Fe(II) has been detected in solution in some of the experiments performed under illumination (see Table 2). Fe(III), which has also been detected, could be formed by homogeneous oxidation of Fe(II) in solution, although direct dissolution of the iron oxide cannot be excluded. Since lattice Fe(III) and adsorbed oxygen compete to excavenge the electrons, a large concentration of iron species would be expected when oxygen is not present. This point has been confirmed in experiments performed under nitrogen atmosphere. The formation of $O_2{}^{\cdot -}$ species is the first step in generating a series of oxidants (e.g., $HO_2{}^{\cdot -}$, H_2O_2, $HO^{\cdot}$) that can oxidize Fe(II) or $SO_3{}^{2-}$ [17]. Conversely, the anion $SO_4{}^{2-}$ has been detected in solution in practically all the experiments. However, the observed amounts of $SO_4{}^{2-}$ in solution are lower than expected from the stoichiometry of the process. Strong adsorption of sulfate anions on the semiconductor surface can account for this fact.

Some experiments using maghemite and magnetite have also been carried out. The yield of sulfite photooxidation in presence of either of those iron oxides is significatively lower than in presence of hematite. After 45 min of irradiation of a 1 mM sulfite solution, only 27% and 34% of this compound is oxidized in presence of maghemite and magnetite, respectively. On the other hand, it must be pointed out that no Fe(II) or Fe(III) has been detected in solution after irradiation.

In order to find an explanation for this last behaviour, two Mössbauer spectra of the maghemite sample at room temperature have been produced for two different experimental situations. The first one correspond to maghemite before irradiation (Fig. 3(a)), and a well defined sextet with the expected spectral parameters is observed (Table 4). Maghemite has an inverse spinel structure, with the Fe(III) distributed 37.5% in tetrahedral sites and 62.5% in octahedral sites [18]. The spectrum of Fig. 3(b) was taken to a maghemite sample after the photocatalytic process. The spectrum corresponds to what can be expected when analysing a mixture of maghemite and magnetite. The spectral parameters used to fit the subspectra assigned to maghemite were those used in Fig. 3(a). The two other subspectra used for an optimal fit can be assigned to

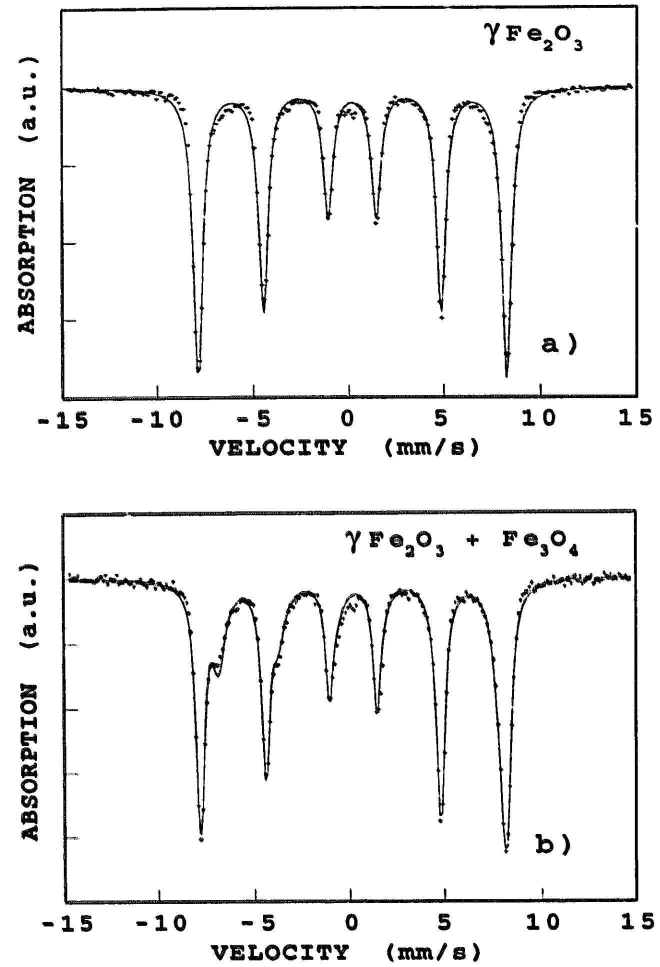

Fig. 3. Mössbauer spectra at room temperature. The dots represent the experimental data and the solid lines computer fitted spectra. (a) maghemite, and (b) maghemite after being used as photocatalyst. The spectrum could be decomposed into three sub spectra that could be assigned to a mixture of maghemite (≈43% and magnetite (≈57%).

Table 4
Mössbauer spectral parameters of the maghemite sample alone and the maghemite + magnetite sample obtained after photocatalysis

	Mössbauer parameters at room temperature			
	Possible site A(tetragonal) B(octahedral)	Isomer shift [a] (mm/s)	Quadrupole splitting (mm/s)	Internal magnetic field (Tesla)
γ-Fe_2O_3	Fe^{3+}(A+B)	0.32±0.04	0	49.9±0.2
Fe_3O_4	Fe^{3+}(A)	0.32±0.04	−0.05±0.01	48.7±0.4
	$Fe^{2+,3+}$(B)	0.62±0.02	−0.01±0.01	45.4±0.4

[a] The isomer shift values are relative to α-Fe.

magnetite, Fe(II)Fe(III)$_2$O$_4$, where Fe(III) are half in octahedral and half in tetrahedral sites, and Fe(II) are only in octahedral sites, with continuous electron hopping between the Fe(II) and Fe(III) in octahedral positions [19], (Table 4). These results suggest that part of the γ-Fe$_2$O$_3$ suffers a solid-state phase transformation to magnetite, Fe$_3$O$_4$. It is noteworthy that if a sample contains a wide particle size distribution, the lines from particles with different sizes will not suffer the same isomer shift, and the line width of the Mössbauer spectrum will then be broaden in an asymmetrical way, as it is most likely the case in our microcrystalline samples.

Indeed, the crystalline structures of maghemite and magnetite are very similar (inverse spinel) and, consequently the Fe(III) in the octahedrical position can be readily reduced to Fe(II) without a large lattice distortion [16]. Clearly, Fe(III) is reduced, but instead of being released into the solution, it remains incorporated in the crystalline lattice.

4. Conclusions

The oxidation of sulfite in aerated water suspensions is photocatalyzed by the presence of hematite particles. The mechanism of oxidation seems to be related to the electron transfer between the S(IV) of the adsorbed sulfite and the Fe(III) of the surface of the hematite particles, yielding both sulfate ions, which strongly adsorb on those surfaces, competing with the sulfite for the adsorption sites, and some Fe(II) species which readily dissolve.

Maghemite and magnetite are less powerful catalysts for the oxidation of sulfite. In those cases it seems that the reduction of Fe^{3+} to Fe^{2+} does not imply the dissolution of the second species. Instead, a sort of solid state phase change takes place where only the Fe^{3+} ions situated in octahedral sites become reduced and remain "in situ" leading to the local formation of the crystal structure of magnetite.

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