

## Advanced vibrational spectroscopy of magnetite nanoparticles

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**Abstract.** In this work, we discuss the challenges associated with measuring and interpreting the vibrational properties of nanomaterials at mid- and far-infrared frequencies, where vibrational bands are often broad and overlapping. This issue is compounded by the complex interaction between infrared light and particulate samples, which depends on packing density and particle connectivity. Preliminary results concerning the far-infrared optical properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been obtained using the two most reliable methods (specular reflectance and attenuated total reflectance). These results are compared to one another and to their Raman counterparts. Finally, the influences of particle size and composition on the vibrational spectra are qualitatively discussed.

### 1 Introduction

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles are of great interest in biomedicine due to their high saturation magnetization and magnetic anisotropy, which makes them a promising candidate for magnetic hyperthermia. The development of this technology requires producing magnetite nanoparticles with a narrow size distribution and good compositional control. This last point is particularly complex, due to the tendency of magnetite to oxidize into maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). The characterization of these products by methods based on diffraction techniques is complicated due to the great similarities between iron oxide phases, so the reference method is Mössbauer nuclear spectroscopy.

In this contribution, we want to explore the possibility of using vibrational spectroscopies to study multi-phase iron oxide nanoparticles in a quantitative manner. These techniques are usually thought of as qualitative characterization tools in nanoscience. In the case of infrared spectroscopy, in particular, the difficulty of extracting useful data from measurements stems from the need to use sophisticated mathematical processing tools, as well as the low reproducibility between different techniques [1].

The goal of this contribution is to explore the possibility of extracting relevant information about the structure and composition of magnetite samples using two reflectance-based infrared spectroscopic techniques, discuss their measurement and interpretation challenges, and to compare their results to those of Raman spectroscopy.

### 2 Materials and methods

The samples were synthesized by thermal decomposition of iron(III) oleates [2], yield high-quality magnetite nanoparticles with diverse sizes and morphologies. Two samples, with average diameters of 37 nm and 13 nm, have been selected for this work. The bigger particles show an octahedral morphology with low polydispersity, whereas the smaller ones are spherical with a larger size dispersion (~ 20%).

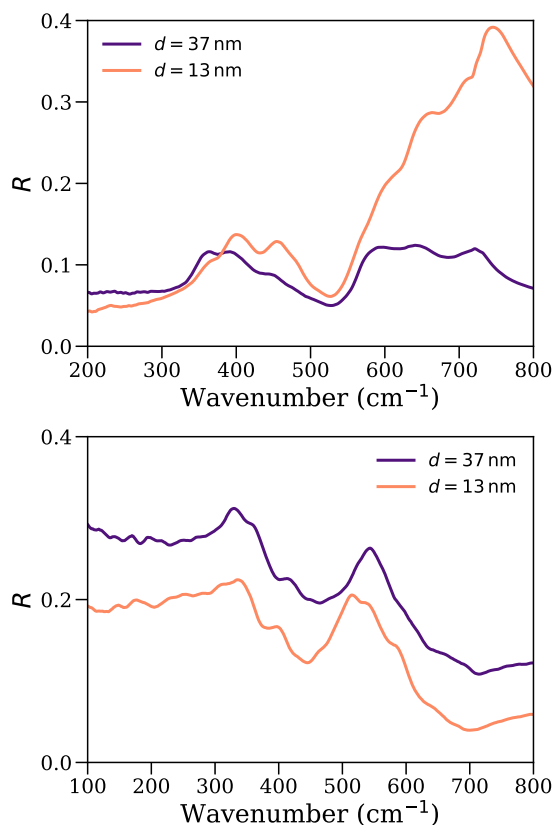
Infrared spectra were acquired using two methods: a single-bounce ( $\theta = 45^\circ$ ) attenuated total reflectance (ATR) system with diamond as internal reflection element, and a specular reflectance (SR) accessory ( $\theta = 15^\circ$ ). A small amount of powder was placed directly on the ATR crystal, whereas pressed pellets were required for the SR instrument, in order to produce a specular surface.

Raman spectra were acquired with an excitation wavelength of 633 nm and 5 mW power, to avoid inducing further oxidation on the samples [3]. The baselines were corrected using the concave rubber-band algorithm implemented in the OPUS program (Bruker).

### 3 Results and discussion

The results of the infrared characterization are shown in Figure 1. Reflectance spectra obtained using the ATR method are shown at the top, with the SR ones at the bottom. It must be noted that these measurements cannot be directly compared. Not only are the angles of incidence different, but the reflectance obtained in the ATR geometry is obtained indirectly through processing the directly

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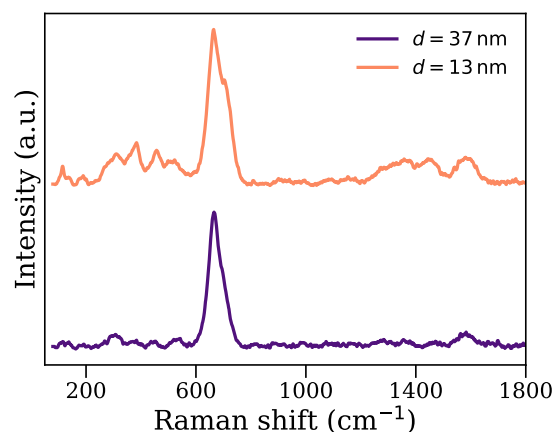


**Figure 1.** Infrared reflectance measurements of pressed magnetite powders. Top: reflectivity obtained indirectly from ATR absorbance measurements at  $45^\circ$ . Bottom: specular reflectivity measured directly at  $15^\circ$ .

measured quantity, the absorbance. In both instances, similar sets of vibrational bands are observed in the  $300 - 600 \text{ cm}^{-1}$  range, with larger differences at higher frequencies. Moreover, the SR measurements seem to reveal more clearly the presence of small bands in the  $100 - 300 \text{ cm}^{-1}$  range. This might be attributed to the use of a very sensitive bolometer to perform far-infrared SR measurements.

Raman spectra of the samples were collected for completeness (Figure 2). As expected, the main peak around  $700 \text{ cm}^{-1}$  dominates the spectrum of the bigger particles, presumably closer to fully stoichiometric magnetite [4]. In both instances, small bands at higher and lower frequencies, as well as a shoulder of the main band, are observed, although they are much less intense for the 37 nm sample.

Indexation and assignment of vibrational modes for iron oxides remains controversial, with little progress compared to calculations and systematic reviews published decades ago [3–5]. In our case, the presence of a plethora of small modes in both the infrared and Raman spectra suggests that the data cannot be well-described by simple crystal structures, and thus more theoretical work is required. Furthermore, differences in both infrared measurements reveal that these measurements cannot be taken at face value and require modeling through explicit consideration of light-matter interaction for granular materials at different densities and geometries [1].



**Figure 2.** Baseline-corrected Raman spectra of pressed magnetite powders.

## 4 Concluding remarks

Important differences are observed between the vibrational spectra of each sample, which are attributed mainly to differences in stoichiometry. The spectra obtained from each of the infrared reflectance techniques show discrepancies that must be accounted for in a model of the interaction between infrared radiation and nanoparticles in each experimental condition. The results suggest that vibrational spectroscopies can be powerful analytical tools for these materials, although light-matter interaction models are still required for a quantitative interpretation of the data.

## 5 Acknowledgments

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