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The role of zinc white pigment on the degradation of shellac resin in artworks

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Abstract: The stability and degradation behavior of natural resins, shellac in particular, have been investigated by many authors for their important role in conservation chemistry but resin compositions and related degradation issues are not completely understood. In this work some results of an extensive investigation on stability under thermal and photo-oxidative ageing of natural materials employed in the field of artistic production and artworks conservation are presented, and in particular the ageing behaviour of shellac in presence of zinc white (ZnO) is described. This work underlines the importance of natural resins / pigments interactions from the point of view of the conservative behavior of paintings since their the decaying paths may be dramatically affected. During the photo-oxidative ageing of zinc white and shellac mixtures the formation of zinc oxalate has been also detected. The formation of oxalates and the different degradation products from natural resins in presence of pigments are of particular interest considering the way the different degradation processes (double bond formation, ester formation, hydrolysis and polymerisation) and the new chemical species (oxalates, metal soaps) can affect the removability of layers and, more generally, the cleaning processes, modifying in many cases the boundary between painting and varnish layers, and the aesthetical aspects of the work surfaces.

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To
Matija Strlic, UCL Centre for Sustainable Heritage
Katherine Curran, UCL Centre for Sustainable Heritage
Guest Editors
Polymer Degradation and Stability Special Issue
Polymers in Art and History – Deagradation and Stabilisation

Dear Editors,

I am submitting a typewritten manuscript entitled “THE ROLE OF ZINC WHITE PIGMENT ON THE DEGRADATION OF SHELLAC RESIN IN ARTWORKS”, for publication in the special issue of PDS on Polymers in Art and History.

The paper is a contribution resulting from the cooperation of prof. Chiantore’s group and the Center for Conservation and Restoration *La Venaria Reale*, and contains original results from a research project which is under development.

We hope the proposed subject and the results could be appropriate for this special issue of PDS.

Kindest regards,
Oscar Chiantore and Tommaso Poli

THE ROLE OF ZINC WHITE PIGMENT ON THE DEGRADATION OF SHELLAC RESIN IN ARTWORKS

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ABSTRACT

The stability and degradation behavior of natural resins, shellac in particular, have been investigated by many authors for their important role in conservation chemistry but resin compositions and related degradation issues are not completely understood. In this work some results of an extensive investigation on stability under thermal and photo-oxidative ageing of natural materials employed in the field of artistic production and artworks conservation are presented, and in particular the ageing behaviour of shellac in presence of zinc white (ZnO) is described. This work underlines the importance of natural resins / pigments interactions from the point of view of the conservative behavior of paintings since their the decaying paths may be dramatically affected. During the photo-oxidative ageing of zinc white and shellac mixtures the formation of

zinc oxalate has been also detected. The formation of oxalates and the different degradation products from natural resins in presence of pigments are of particular interest considering the way the different degradation processes (double bond formation, ester formation, hydrolysis and polymerisation) and the new chemical species (oxalates, metal soaps) can affect the removability of layers and, more generally, the cleaning processes, modifying in many cases the boundary between painting and varnish layers, and the aesthetical aspects of the work surfaces.

KEYWORDS

Shellac, zinc white, natural resins, oxalates, FT-IR

INTRODUCTION

Natural resins are polymeric substances commonly and widely employed in the Cultural Heritage field and in conservation as finishing layers or varnishes, for their appreciated optical and preservative properties. In many cases they have been used mixed with drying oils in order to obtain oleo-resinous binders with particular aesthetical properties, or else pure as binders in retouching paintings. In all these applications the resins come in contact with pigments by direct mixing or by interaction with the underneath painting layer often impoverished by natural binder migration. Moreover the usual conservative treatments for varnish substitution place fresh natural resin in contact with painting pigments increasingly exposed as consequence of previous solvent based cleanings. Shellac, in particular, is the most used and appreciated finishing in historical wooden furniture [1, 2] but it has been also used by many artists as painting varnish mixed with other softer resins [3]. Chemically, shellac is a complex mixture of mono and polyesters

coming from hydroxy aliphatic acids (mostly aleuritic acid) and many different cyclic sesquiterpene acids [4-10].

In this work, some results of an extensive investigation on stability of natural materials employed in the field of artistic production and artworks conservation will be presented, and in particular the ageing behaviour of shellac in presence of zinc white (ZnO) will be described. It is well known that the presence of pigment influences dramatically the response of polymers and resins towards thermal and photo-oxidative stresses [11].

Mixtures of a large number of painting binders and varnishes (drying oil, natural resins, proteinaceous binders) with the most common historical pigment, in different ageing conditions (photo-oxidative, thermal oxidation -60 C°- and thermal degradation -300 C°-), have been studied in order to evaluate the influence of inorganic pigments in the degradation processes of organic materials such as the formation of metal carboxylates, as described in literature [12-15].

ZnO is a widely diffused white pigment (zinc white or chinese white) introduced in the second half of the 18th century; it can be easily found also as additive or as co-pigment such in the case of titanium white in order to modify the film-forming properties in particular in presence of drying oils: commercial titanium whites often contain a percentage of ZnO in order to enhance the stiffness of the painting layers [16]. Zinc white is a very active pigment and its ability to easily react with free carboxylic acids present in the oil binding media to form zinc soaps is well assessed [15, 16]. This issue however is very delicate because the presence of zinc carboxylates on an easel painting cannot always be associated with a degradation process since commercial formulation may contain zinc stearate as an additive. This research highlights that even natural resins can produce metal soaps, in particular zinc soaps, and confirm that at the interface

painting/ varnish layer a competition between carboxylic acids from drying oil and resin acids becomes possible.

To investigate the different ageing and oxidative behaviors of shellac in the presence of zinc oxide FTIR is a particularly suitable technique because of the minimal interference coming from zinc white that does not present significant absorption signals in most of the medium infrared spectral range, with the metal/oxygen band raising only below 600 cm^{-1} .

During the photo-oxidative ageing of zinc white and shellac mixtures the formation of zinc oxalate has been also detected. This finding was unexpected and clearly indicate that oxidation of natural resin layers can be a suitable source of oxalate patina.

The most common way to find oxalates in the field of Cultural Heritage is on carbonatic stone materials exposed outdoor and on mural paintings [17-20]. The presence of calcium oxalates (wewellite and weddellite, the monohydrated and dihydrated form respectively) on monuments appears with different “faces”: as unhomogeneous alteration, as first layer of the black crusts and as the so called “patina nobile”. The origin of this decaying process is still unknown even if some hypothesis have been proposed. Three are the more speculated suggestions and they are all related to the identification of the oxalic acid source [21-25]:

- oxalates come from bioweathering processes involving the reaction between the carbonatic substrate and the oxalic acid produced by biological subjects such as algae, fungi or bacteria.
- oxalic acid is the final step of decaying processes, such as strong oxidative reactions, of organic materials applied on the stone substrate with aesthetical, protective or consolidating purposes.

- oxalates come from the interaction between the calcite and the free oxalic acid present in the environment

All these proposal are mostly suitable and applicable in the case of outdoor exposed artifact; however, calcium and other oxalates are found even in the case of easel paintings or other polychrome art works reasonably never exposed to outdoor environment or to strong oxidative agents and without any detectable microbiological presence [26-28]. Most of the times, calcium oxalates in easel paintings have been detected on substrates in contact with proteinaceous compounds such as animal glue used for ground preparation or in a conservative interventions [29].

In this work we demonstrate that oxalates (in this specific case zinc oxalate) are formed as decay product from mixtures of resin and pigment submitted to photo-oxidative ageing. The possibility of formation of oxalates by means of strong oxidative conditions has been experimented only for organic binders, such as linseed oil and egg, on calcium carbonate substrate [30] but never, in our knowledge, in presence of natural resins or other cations and, most important thing, never in weak oxidative conditions.

The formation of zinc oxalates has been assessed by means of FTIR transmission measurements and X-ray diffraction on aged laboratory mockups and it has been also corroborated with findings on a painting by the futurist artist Giacomo Balla where the painter had used an oleoresinous binder [31].

The formation of oxalates and the different degradation products from natural resins in presence of pigments is of particular interest considering the way that the different degradation processes (double bond formation, ester formation and polymerisation) and the formation of new chemical species (oxalates, metal soaps, etc etc) can affect the

removability and the cleaning processes, modifying in many case the boundary between painting layer and varnish, and the aesthetical aspects of the work surfaces.

MATERIALS AND METHODS

Shellac and zinc white, a pure zinc oxide pigment, were supplied by Kremer GmbH & Co. Methanol (Aldrich) solutions of Shellac and of the mixture shellac/zinc white (1:1 in weight) have been applied by brush on polished silicon wafers.

Four sets of samples have been aged in the following ways:

- 2 years at room condition with no direct light exposition
- 1000 hours in oven at 60 C°
- 3 minutes at 300 C° on a heating plate
- 1000 hours in an UV solar box Hereus Suntest CPS equipped with a filtered (Coated quartz glass simulating a 3mm window glass, $\lambda < 300$ nm) Xenon lamp and with an average irradiation of 750 W/m² and an internal temperature of about 50 C°.

FT-IR transmission spectra (64 scans) recorded using a diamond anvil cell (High Pressure Diamond Optics, Inc.) were obtained on a Bruker Vertex 70 spectrophotometer coupled with a Bruker Hyperion 3000 IR microscope equipped with an MCT detector (Infrared Associates Inc.), working in the spectral range from 4000 to 600 cm⁻¹ with an average spectral resolution of 4 cm⁻¹.

X-ray diffractometry analyses have been carried out on a Panalytical X'Pert PRO X-ray powder diffractometer (XRPD) equipped with an X'Celerator detector PW3015/20 and diffraction patterns have been collected from 5° to 60° 2 θ , scan speed 0.21° s⁻¹, with a

CuK α -radiation source, working conditions 40 kV and 40 mA. Powdered samples have been spread on an amorphous silicon holder and then analyzed.

RESULTS AND DISCUSSION

The stability and degradation behavior of natural resins, shellac in particular, have been investigated by many authors [4, 6, 7, 10, 32-37] for their important role in the conservation chemistry but compositions and related degradation issues are not completely understood.

The degradation behavior of pure shellac under the applied ageing conditions is in the following compared with results reported in the literature. The infrared spectrum of shellac is shown in Figure 1 (spectrum I) where it is compared with the spectra of the same resin after photo-oxidative (1000 h) and after thermal (3 min at 300 C°) ageing.

The carbonyl absorptions from 1650 to 1800 cm⁻¹, the oxydrylic broad band around 3400 cm⁻¹ and the band at 1252 cm⁻¹ are clearly affected by the different ageings.

The unaged shellac shows a triple carbonyl stretching signal (Fig. 2, spectrum I), with maxima at 1688, 1711 and 1734 cm⁻¹ attributable to the alicyclic sesquiterpene free acids, the aliphatic hydroxy acids (mostly aleuritic acid) and the complex mixture of mono and polyesters respectively.

After the strong thermal ageing (Fig. 1, spectrum II) there is a rising of the esteric signal while the signal of acids decreases, in particular the one at 1688 cm⁻¹ seems to disappear (Fig. 2, spectrum II). This behaviour is consistent with the decrease of the oxydrylic bands at 1252 cm⁻¹ and around 3400 cm⁻¹: the high temperature promotes the inter-esterification of acid function with the OH groups of aleuritic acid and similar hydroxy acids, and eventually with remains of alcohol used as solvent.

On the other hand the thermal ageing at 60 °C does not affect significantly the shellac: the spectrum (not here reported) is very similar to the unaged one.

After the photo-oxidative ageing, a carbonyl band trend similar to the thermal aged one is observed but the important shoulder at 1770 cm^{-1} suggests that also an intramolecular esterification has taken place with the formation of lactone compounds (Fig. 2, spectrum III).

Chromatographic studies suggest that the amount of aliphatic hydroxy acids, consumed by esterification and lactonisation, should be definitely lower but the acid carbonyl signal only slightly decreases because a partial de-esterification of the polymeric backbone takes place and previously bonded acids become available [10].

This new available hydroxy acids participate to the creation of a three-dimensional structure responsible of the resin solubility reduction. In the spectrum of the UV aged shellac (Fig. 1, spectrum III) it is also possible to note the appearing of a sharp signal at 2850 and 2920 cm^{-1} due to the wax component (shellac contains around 5-10% of waxy fraction), only partially deducible from the other spectra. It is important to highlight that after the UV ageing the mockups of shellac layers lost their yellowish-orange shade to become transparent as confirmed by the disappearing of the conjugated double bond signal at 1636 cm^{-1} (Fig. 2, spectrum III).

The addition of zinc white significantly modified the behaviour of shellac submitted to the different ageing conditions. The main differences are clearly seen in the spectral range between 1500 and 1650 cm^{-1} .

After the strong thermal ageing, while the main spectral backbone appears almost unaltered, two new strong bands appear at 1420 and 1590 cm^{-1} (Fig. 3, spectrum II).

These are the bands related to the formation of zinc metal soaps coming from the reaction between the pigment and the resinous acids.

The recorded wavenumbers values and the shape of the two bands are perfectly comparable to the ones known for the zinc metal soap formed from drying oils [14]: this coincidence seems to indicate that aliphatic hydroxy acids are more prone to give the metal soaps than the alicyclic sesquiterpene free acids.

As in the case of pure shellac, ageing at the high temperature favours the formation of esteric structures, as shown by the strong carbonyl band centered at 1734 cm^{-1} . At the high wavenumbers the OH stretching band appears split in two: the usual OH band of shellac at 3420 cm^{-1} and a new band at 3268 cm^{-1} that could be attributed to OH groups interacting with the ZnO centres.

The effect of ZnO on the photo-oxidation of shellac is particularly interesting (Fig.3, spectrum III) since some photo-oxidative protection effect was expected. Beside the formation of the zinc metal soap (in a definitely smaller amount than in the case of thermal ageing) a growth of the band at 1636 cm^{-1} due to carbon-carbon conjugated double bonds takes place. This absorption is probably the responsible of the “pink” coloration that mockups assumed after the photo-oxidative ageing. In the carbonyl spectral range the strongest band remains the one at 1711 cm^{-1} related to the aliphatic hydroxy acids (mainly aleuritic acid). This feature, together with the strong carbonyl signal at 1734 cm^{-1} , due to mono and polyesters, and with the metal soaps formation (all reactions that subtract free acids), seems to confirm that even in presence of ZnO the photo-oxidation promotes a new acid formation through hydrolysis of the backbone polymer, as suggested by Coehlo et al.[10]. Moreover the signal of intra-molecular esterification, related to the formation of lactones, around 1770 cm^{-1} , clearly detectable

in the UV aged pure shellac, is not present here: the pigment promotes the other degradation patterns.

At the high wavenumbers the OH stretching band at 3420 cm^{-1} presents an increased intensity confirming the presence of larger number of oxydrilic functions, moreover the band seems to be intensified also by the presence of another signal at slightly lower wavenumbers. The other absorption, appearing as a shoulder at 3268 cm^{-1} , could be assigned to OH groups influenced by the presence of the oxide.

The spectrum of shellac mixed with ZnO aged 2 years at room conditions (Fig. 4) shows an intermediate situation. Obviously the degradation is lower but both double bonds and metal soaps formation are developing. The photo-oxidative ageing drives the system to the double bond formation and backbone hydrolysis while thermal ageing favors the formation of metal soaps and the esterification without double bond formation. The kinetic, and in many cases also the chemistry of these reaction is not clear and should be related to the catalyst/coordinative behaviour of the ZnO under the different thermodynamic conditions. The complexity of the natural resin composition prevents a clearly comprehension of the involved phenomena. More in depth studies should be carried out on simpler systems such as single alicyclic sesquiterpenic and aliphatic hydroxy acids mixed with pigments.

The FTIR spectra of the photochemically aged mixture also reveal the formation of oxalates, in particular of Zn oxalates. The signals of the etheric band at 1320 cm^{-1} common to many oxalates, the second etheric band at 1364 cm^{-1} and the bending at 824 cm^{-1} typical of the Zn oxalate are present in all the recorded spectra and in the spectrum presented in Figure 5, where the spectral zones of interest are shown in the enlargements, the presence of the new compound is particularly evident.

In addition to the above spectroscopic evidences, the nature of the compound has been confirmed by XRD diffraction analysis (Fig.6) showing the typical inter-planar distance (d) of hydrated Zn oxalate. In Figure 6 the comparison with calcium oxalates is reported. The presence of oxalates allows a clearer comprehension of the infrared spectrum of the aged mixture in photo-oxidative conditions: the oxydrylic band at 3420 cm^{-1} and the double bond band at 1636 cm^{-1} are increased by the Zn oxalate absorption bands at 3382 cm^{-1} (OH stretching of the coordinated water) and at 1624 cm^{-1} (carbonyl stretching) respectively.

The measurements reported in this work show that the formation of oxalates can occur even under “light” oxidative environmental conditions and that natural resins and in particular shellac have to be considered as substrates promoter of the oxalates patina formation on paintings once in contact with an active pigment that can work as catalyst [39]. This phenomenon indeed may occur also in real artworks under natural ageing conditions. We have in fact detected the presence of zinc oxalate in a 1915 Giacomo Balla painting “Grido dimostrazione in piazza del Quirinale” (Figure 7), one of the first works of his futurist period, which we have studied in the occasion of a conservative intervention [31].

The analyses on this painting showed a wide employ of zinc white and the use of an oleo-resinous binder in some areas. The same characteristic signals of the hydrated zinc oxalate, the etheric band at 1364 cm^{-1} and the bending at 824 cm^{-1} , have been detected (Fig. 8) on samples coming from the light green layer. In this case the painting was not varnished but recently the presence of different oxalates under the varnish layer, has been reported [27]. This confirms that the oxalate formation can occur even in sheltered areas, surely not microbiologically active and not directly exposed to the environmental

hazards such as direct sunlight or aerial pollutants. The reaction is probably catalyzed by pigments that favor the degradation of painting binders and varnishes to reactive oxalic acid [40] or promote the coordination of active ionomeric complexes that lead directly to the formation of oxalates [41].

CONCLUSIONS

The complex degradation processes occurring during thermal and photo-oxidative ageing of shellac resin in presence of zinc white (pure ZnO) have been studied and characterized. The paper brings the attention on the importance of natural resin reactivity with pigments from the point of view of the conservative behavior of paintings whose decaying paths may be dramatically affected. It has been shown that photooxidative ageing, in presence of ZnO, forces the system to formation of unsaturations and to backbone hydrolysis, partially altering the saponification and reticulation processes, while thermal ageing favors the formation of metal soaps and the esterification of the acid functions. Intra-esterification reactions, that lead to the formation of lactones clearly observed during the photo oxidative ageing of the pure resin, are inhibited or limited by the presence of the zinc oxide. Moreover, during the UV ageing of the shellac and zinc white mixtures, the formation of zinc oxalates has been obtained in particularly “weak” oxidative conditions. The kinetic, and in many case also the chemistry, of these reaction is not clear and probably related to the catalyst/coordinative behaviour of the ZnO under the different thermodynamic conditions. The complexity of the natural resin composition prevents a clear comprehension of the involved phenomena.

All these results suggest that in the evaluation of the conservative conditions of a varnish layer at the two interfaces (air and painting layer) not only a different exposure to temperature , radiation and pollutants but a different chemistry must be considered. Natural resins, and in particular shellac, can be responsible of the formation of metal soaps and other by-products such as oxalates, suggesting that in many paintings at the painting/ varnish layer interface a competition between carboxylic acids from drying oil and resin acids is active.

The formation of oxalates and the different degradation of natural resins in presence of pigments is particularly interesting considering the way that the different degradation processes can affect the varnish removability in the cleaning processes, modifying in many case the boundary between painting layer and varnish, and the aesthetical aspects. The study of the influence of pigments on the oxidative degradation process of artistic organic materials (binders and varnishes) with particular attention to the natural resins behavior is proceeding with examination of other resin/pigment combinations.

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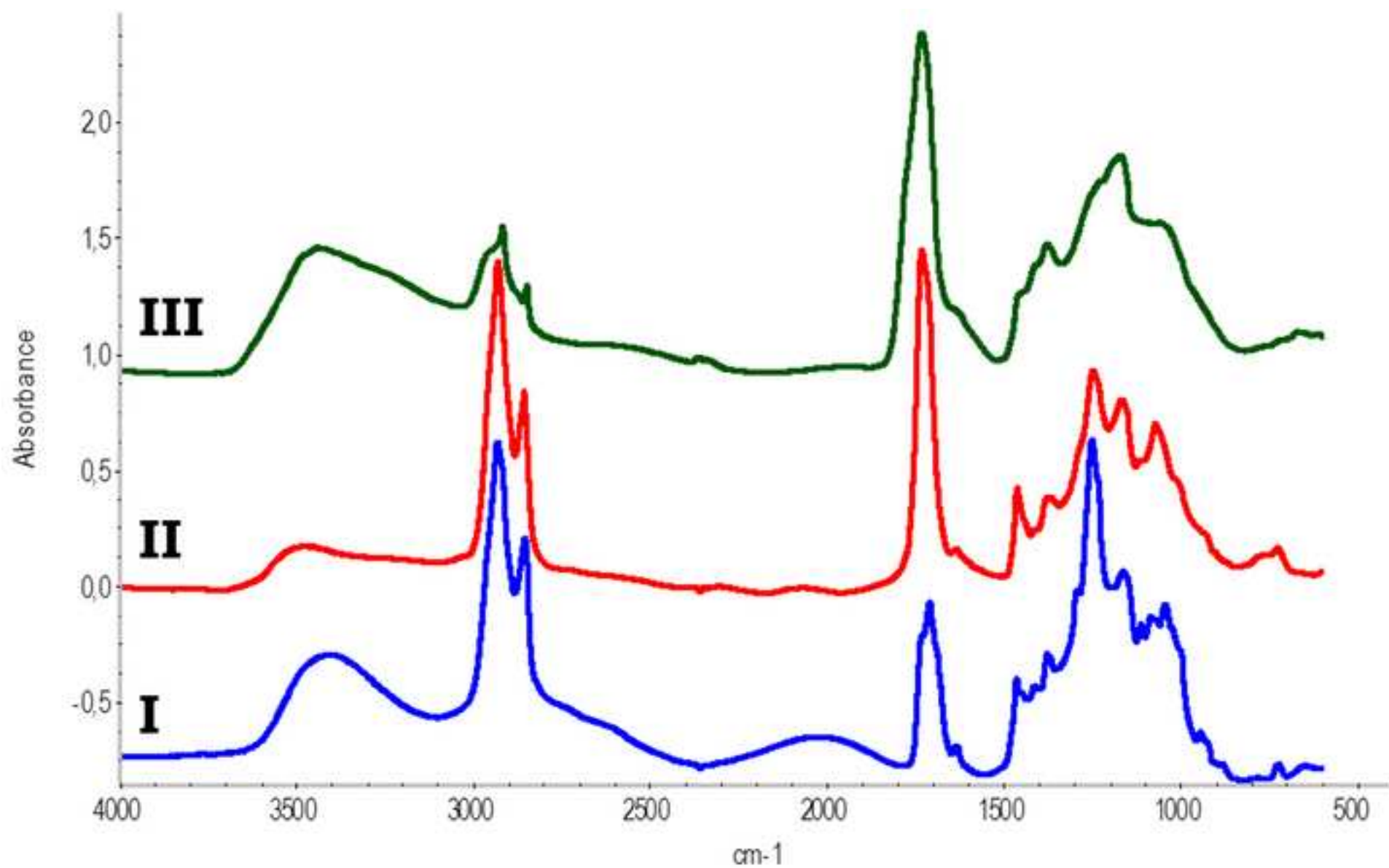


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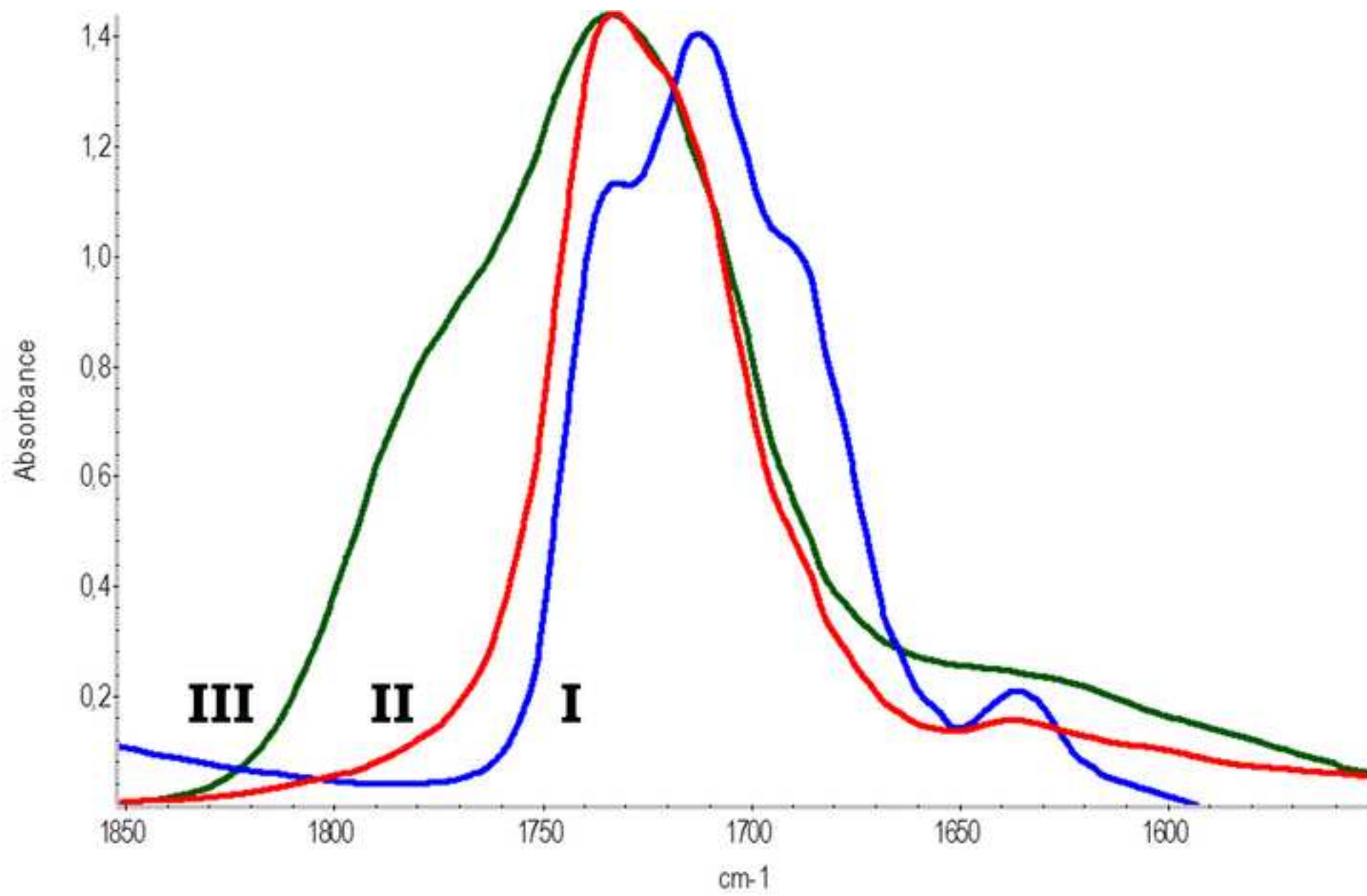


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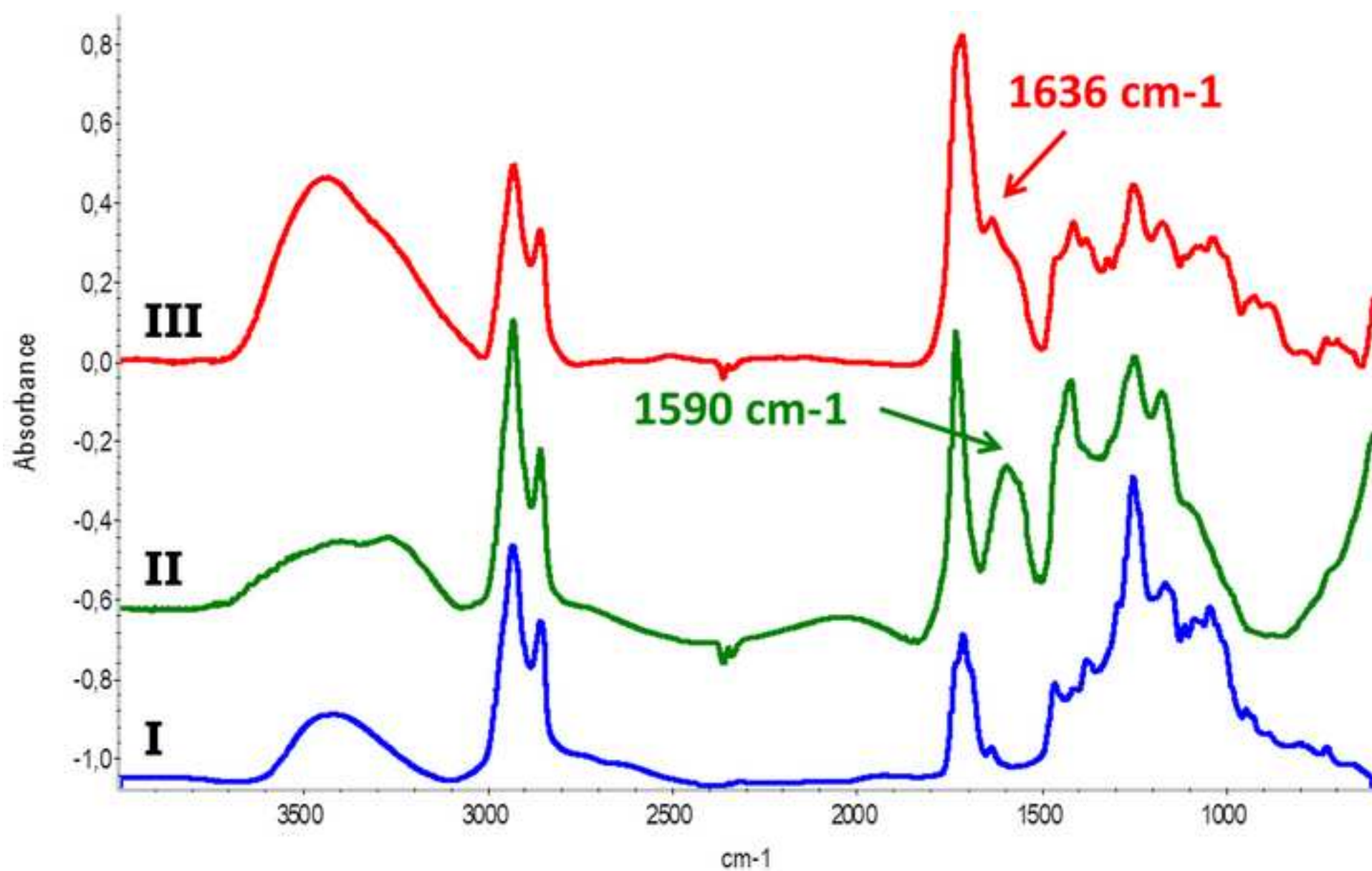


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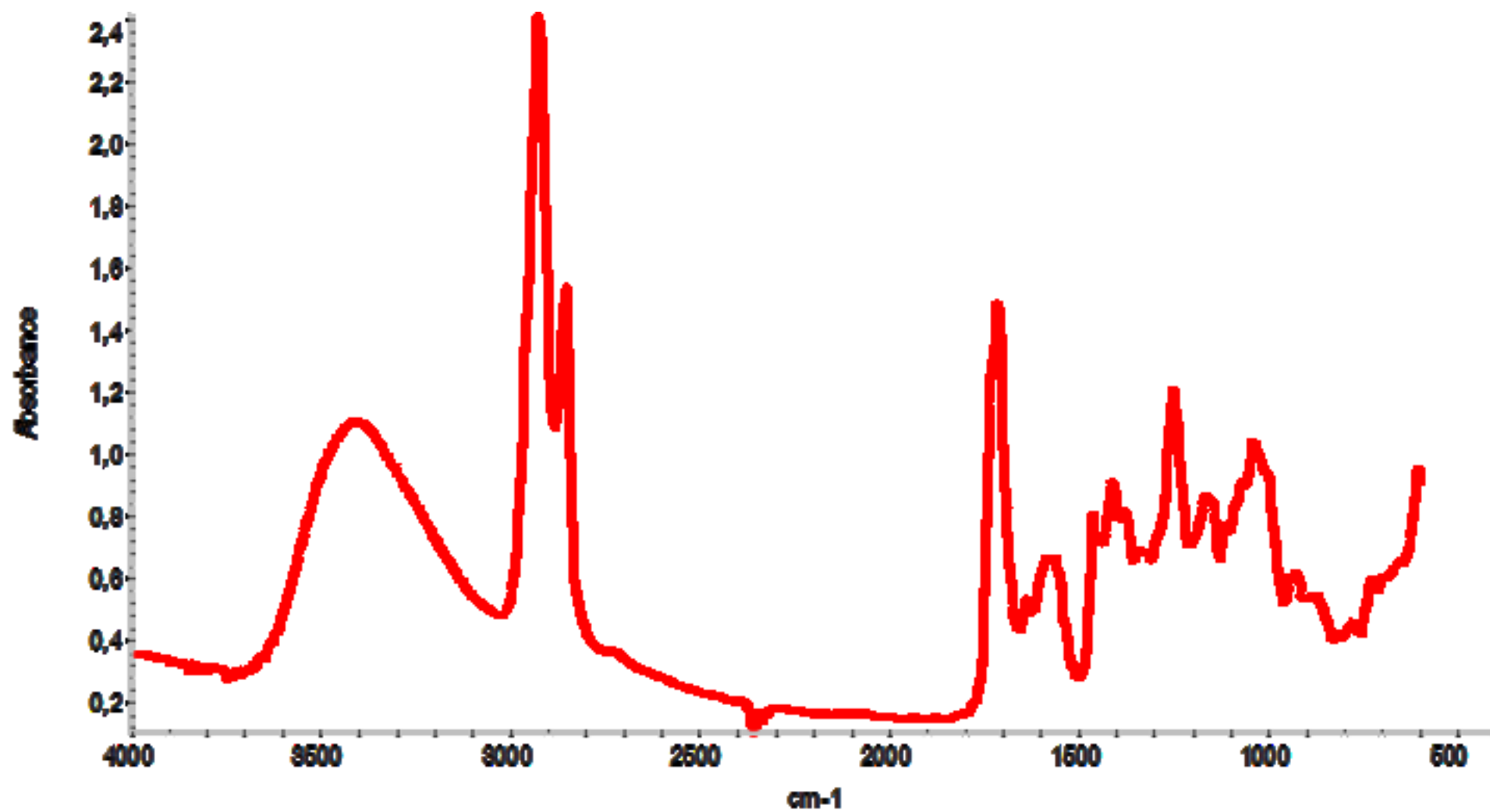


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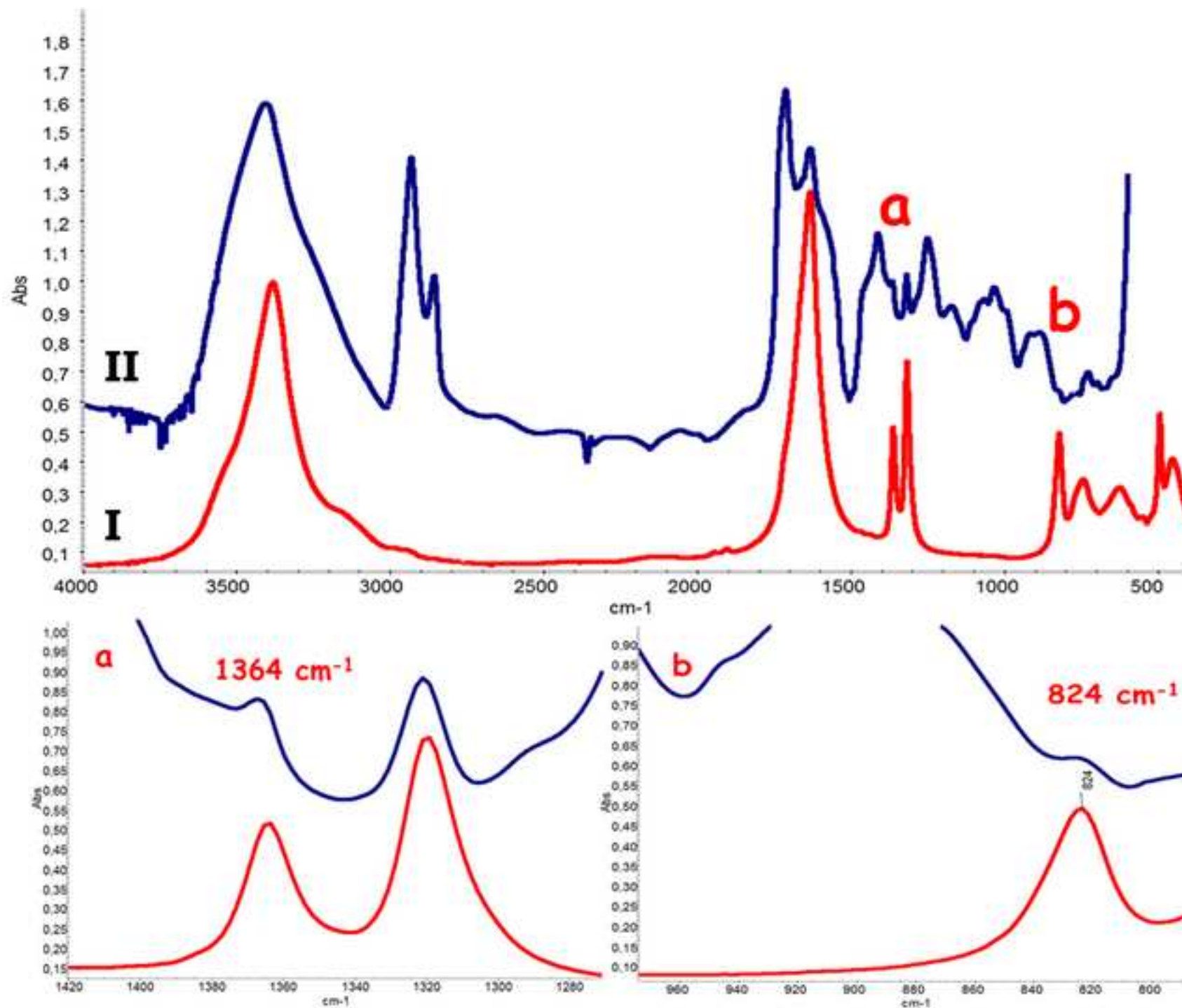


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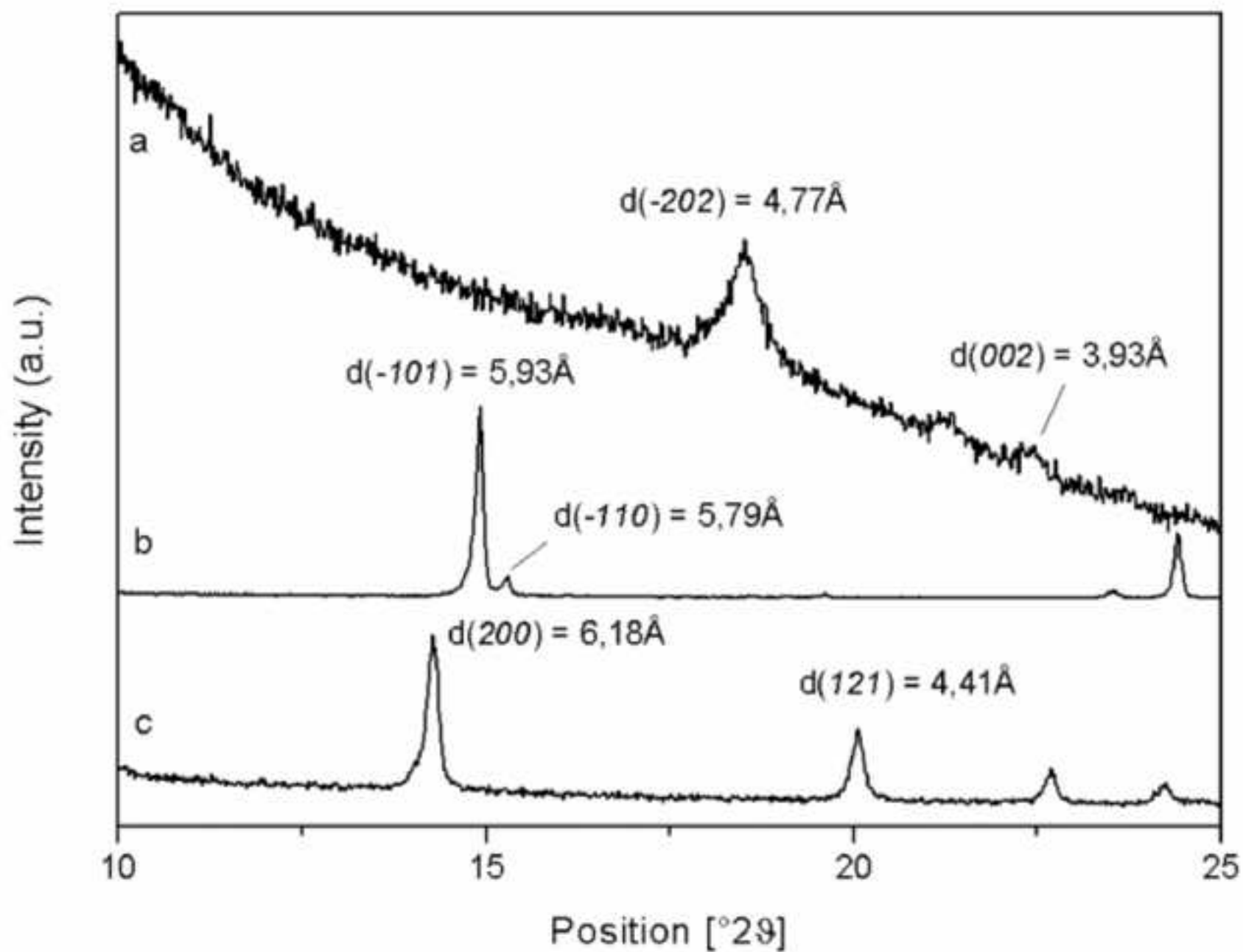


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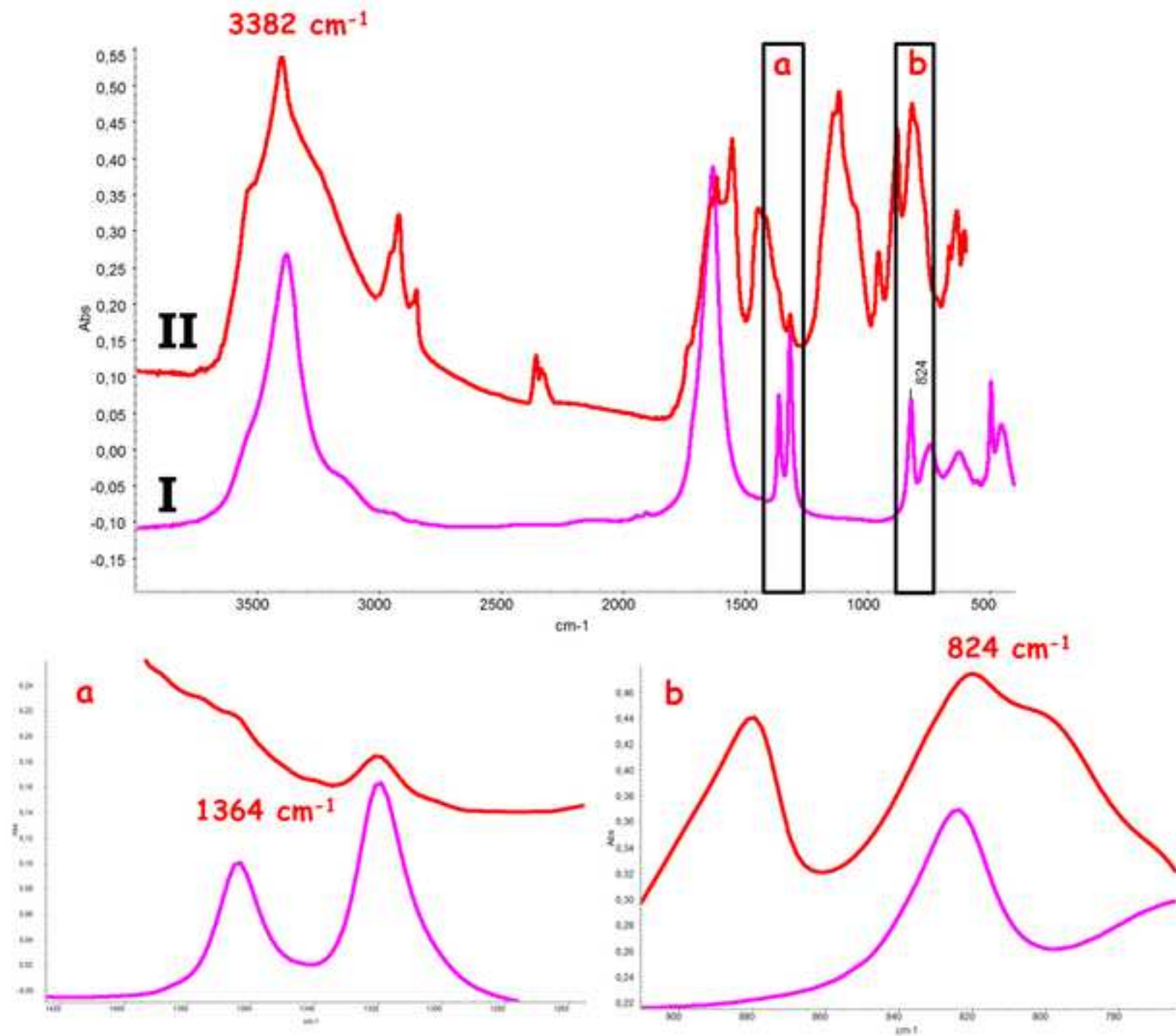


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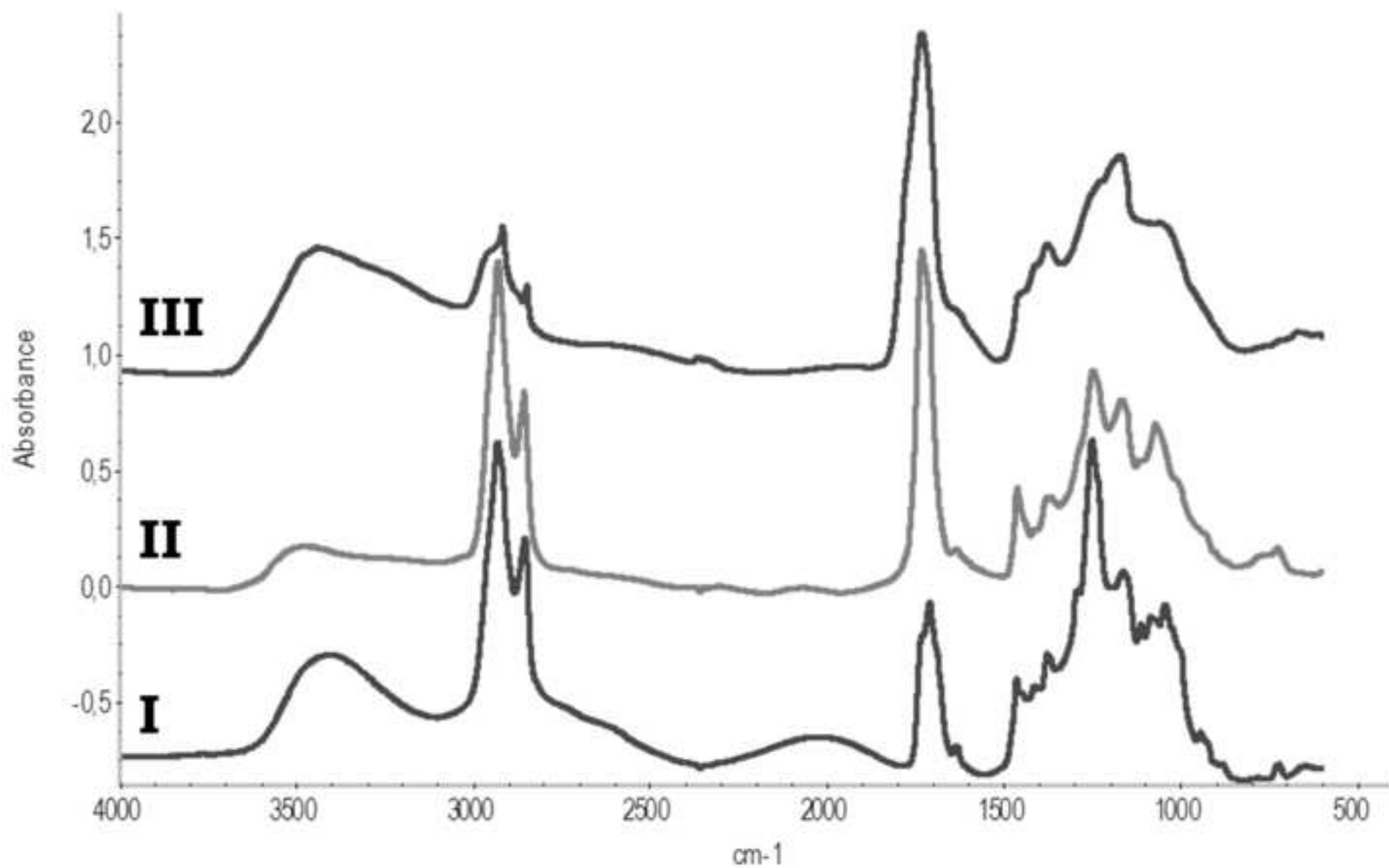


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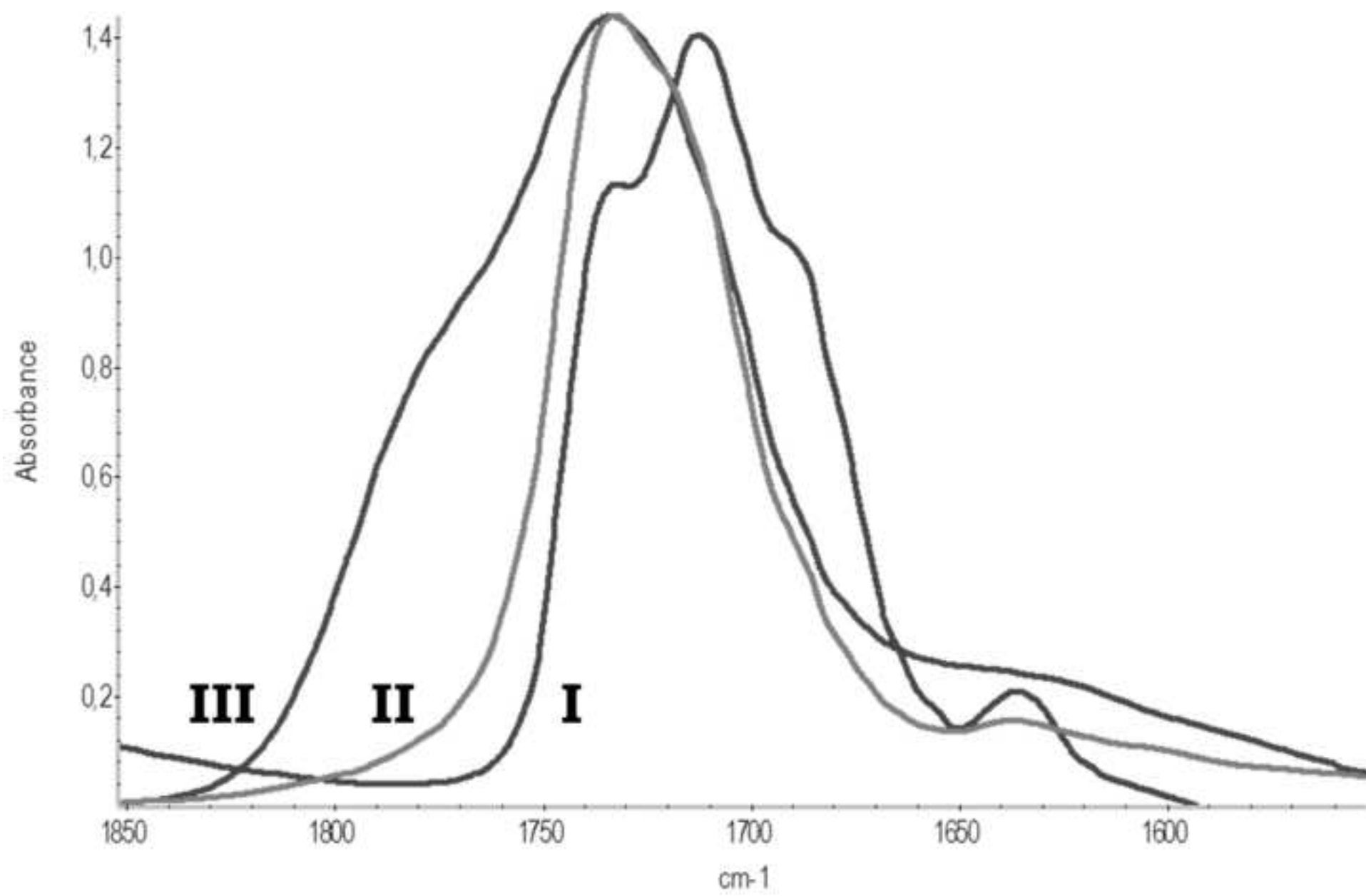


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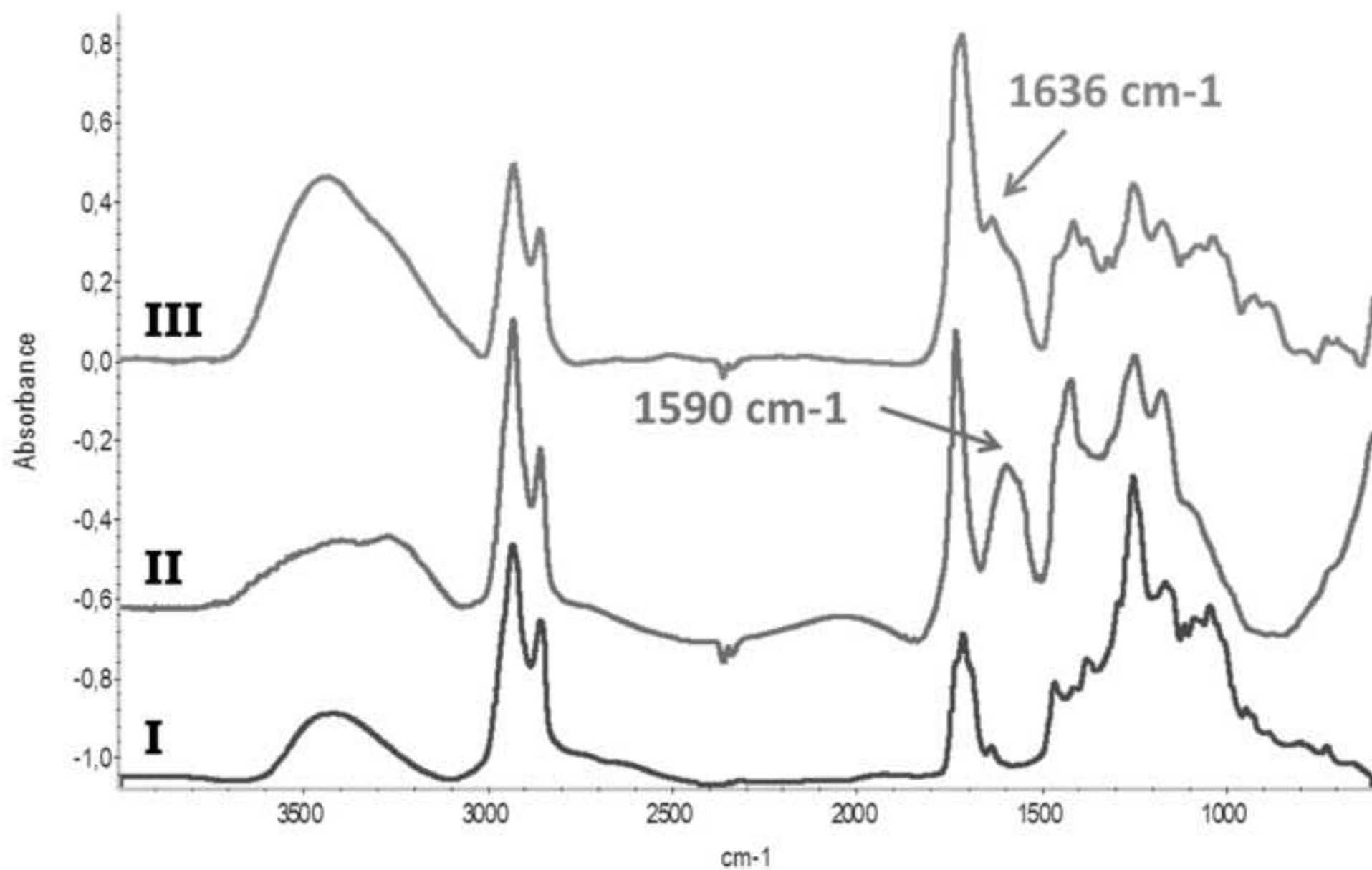


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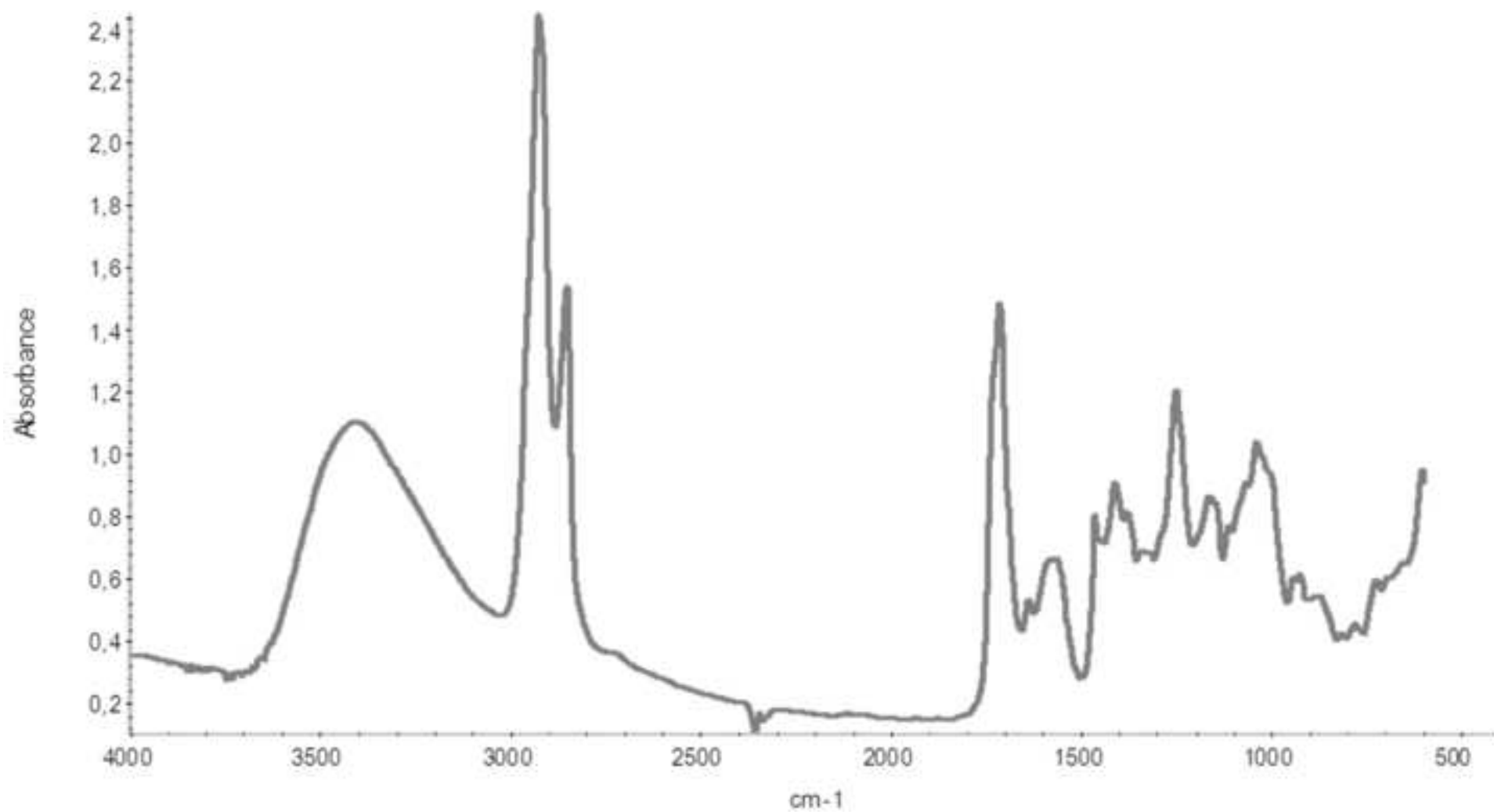


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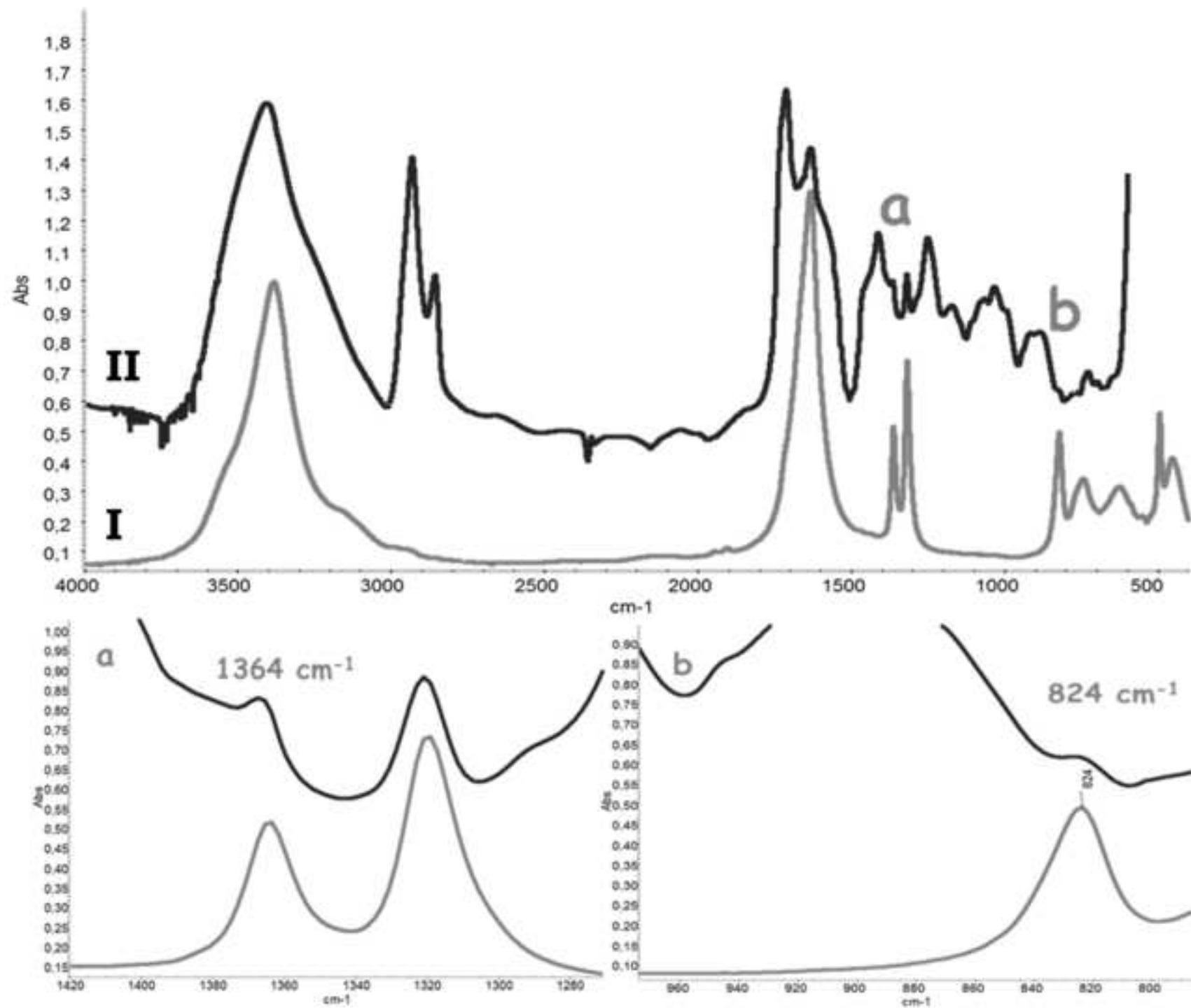


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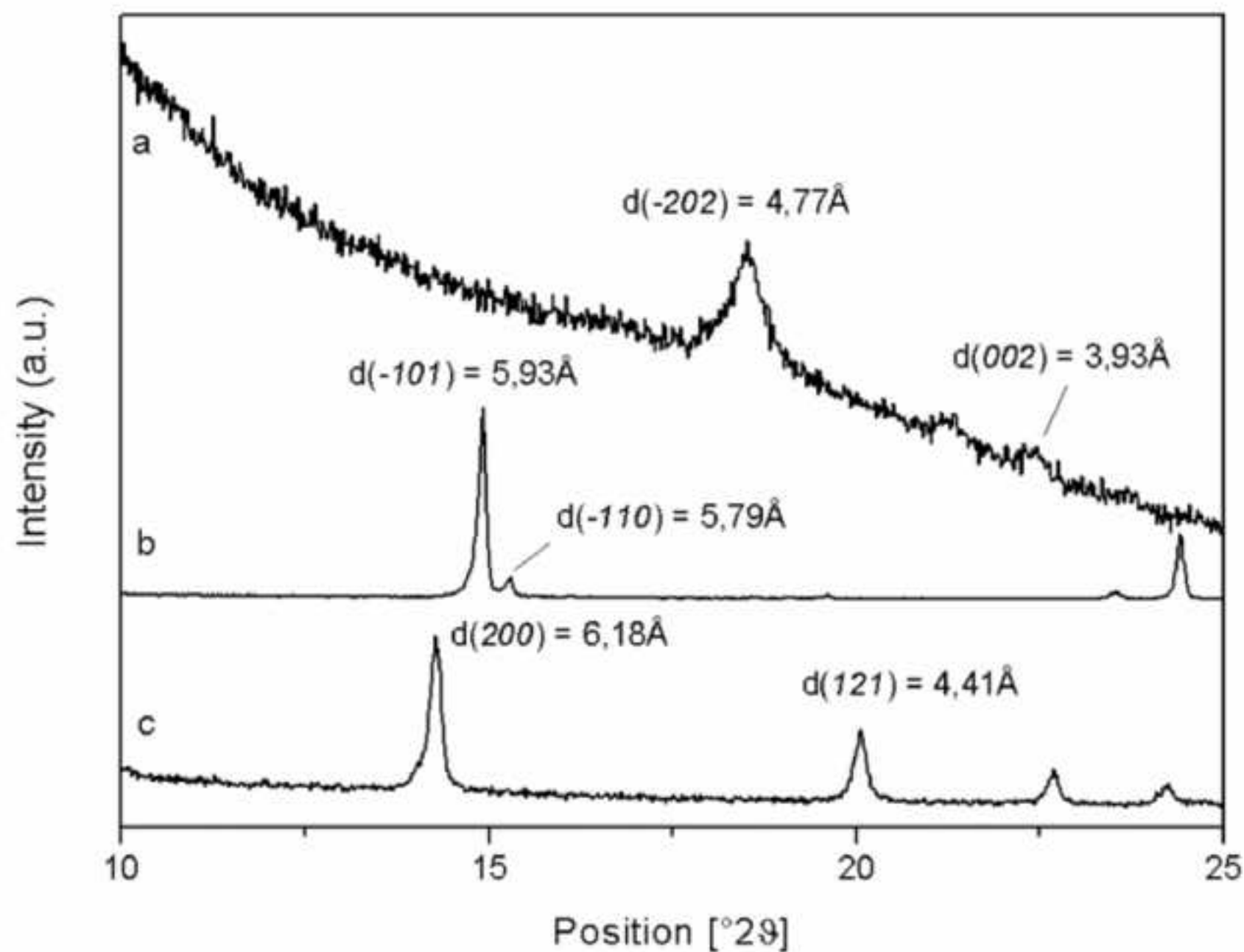


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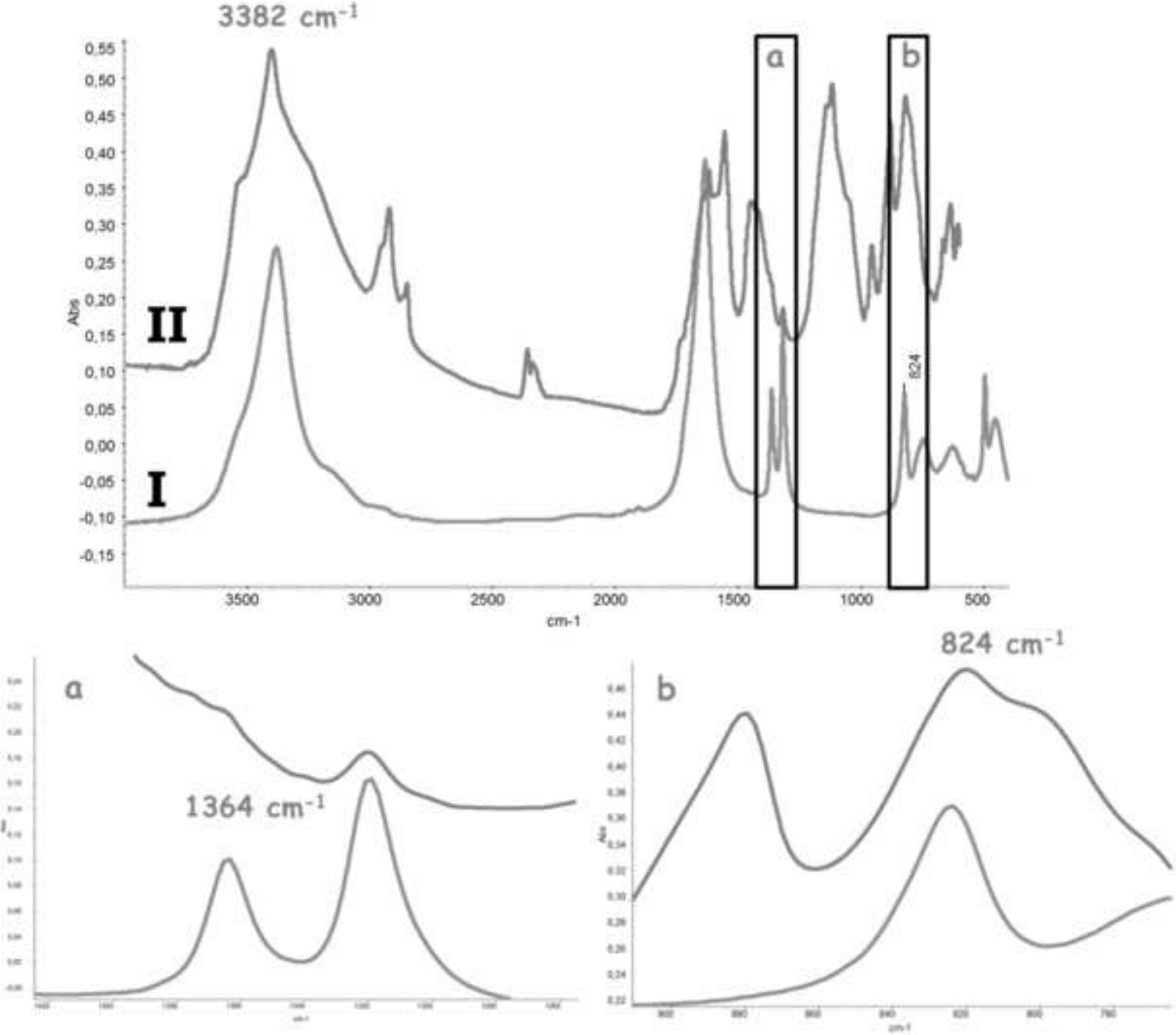


Fig.1 Spectra of shellac before (spectrum I) and strong thermal (spectrum II) and after UV (Spectrum III) ageing, respectively.

Fig.2 Carbonyl bands detail. Spectra of shellac before (spectrum I) and after strong thermal (spectrum II) and photo-oxidative (spectrum III) ageing, respectively.

Fig.3 Spectra of shellac and zinc white mixture before (spectrum I) and after strong thermal (spectrum II) and photo-oxidative (spectrum III) ageing, respectively.

Fig. 4 Spectrum of shellac and zinc white mixture aged 2 years at room conditions.

Fig. 5 Reference spectrum of Zn oxalate (Spectrum I) vs spectrum of the photo aged zinc white/shellac mixture (spectrum II).

Fig. 6 X-Ray diffraction spectra of sample (a), whewellite (b) and weddellite (c) in the 10° - 25° 2θ range. Miller indices, calculated from ICSD (1997), and interplanar distances (d) are reported.

Fig. 7 Giacomo Balla, «Grido dimostrazione in piazza del Quirinale» (1915).

Fig. 8 Reference spectrum of Zn oxalate (spectrim I) vs spectrum coming from a green layer of the Giacomo Balla painting (spectrum II).