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Raman spectroscopic study of some chalcopyrite–xanthate flotation products

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Dedicated to Professor Bernhard Schrader

Abstract

The ability of Raman spectroscopy to investigate chemical substances in water media was applied for studying the surface products of the chalcopyrite–sodium isopropyl xanthate flotation system. Performing the reaction in model conditions, i.e. at high concentration of the collector, led to the formation of copper isopropyl xanthate and diisopropyldixantogen on the chalcopyrite surface. The recorded Raman bands of these compounds were determined on the basis of the vibrational band assignment of normal vibrations of the corresponding individual compounds. The latter facilitated the Raman spectroscopic elucidation of the reaction products formed on the chalcopyrite surface in real industrial flotation conditions with a sodium isopropyl xanthate collector.

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1. Introduction

The separation of minerals from ores is a very important industrial process. The commonly applied separation method is flotation, which ensures the required relation between the hydrophobic and hydrophilic properties on the surface of the mineral particles. This is achieved by adding to the crushed ores, dispersed in water, organic reagents known as collectors. For selective flotation of sulfide minerals, xanthate collectors (ROCS_2^- , where R is an aliphatic radical) are widely employed. Taking into account

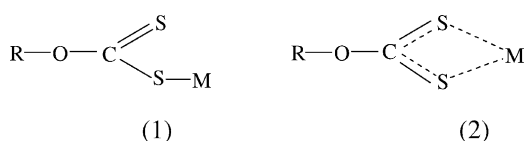
the huge amount of treated raw materials and the incomplete degree of separation, the optimisation of the flotation process is of utmost importance. The study of the composition and structure of the compounds obtained on the mineral surface during the flotation can help to understand its mechanism and to specify the proper conditions for the process that could lead to improvement of the degree of separation.

A distinct progress in identifying the structure of the surface products formed on the mineral surface after the sorption of the collector has been achieved with the aid of spectroscopic methods, especially infrared (IR) spectroscopy. Previous attempts by other researchers were focused on clarifying the character of the metal–xanthate (M–X) bond obtained after

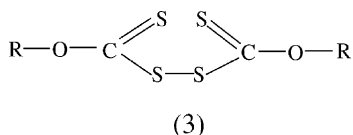
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the sorption of the collector on the mineral surfaces. The alkali-xanthates were known to have an ionic character whereas the chemisorbed xanthates were expected to be covalently bonded with the surface metal. Therefore, the first aim was to determine which of the two limited structures, (1) or (2), elucidate the character of the M-X bond.



Since the obvious difference between structures (1) and (2) is the type of CS bonding, IR spectroscopy has been applied for determining the structure of the metal xanthates. A series of xanthate molecules and compounds with similar structures have been studied using IR with assignment of some of their bands [1]. IR spectra of dioxanthogens (3) as model compounds with CS double bond have also been examined. Further, various IR spectroscopic techniques have been used to study the reaction species formed on the sulfide mineral surfaces during the flotation: diffuse reflectance [2,3], attenuated total reflectance [4-6], external reflectance [7-9], photo-acoustic [10] and gas-phase headspace [11] spectroscopy. Most of these studies ascertained that metal xanthates with structure (2) and the corresponding dioxanthogens (3) are the major surface products obtained by flotation of sulfide minerals. A full vibrational analysis of ethyl and isopropyl xanthates was accomplished on the basis of an ab initio quantum chemical calculation [12].



Until recently the use of Raman spectroscopy for monitoring the composition and the structure of surface flotation products has been very limited despite its several principal advantages over IR. The most important among them is that water solutions and samples in water media can be investigated directly since water bands have low Raman intensity. We pointed out with B. Schrader in a recent paper [13] that the NIR-FT (near infrared-Fourier transformed)

Raman spectra of different crystal modifications can be observed through a layer (about 1 mm) of thermostated water without any visible disturbance to the Raman spectrum. In addition, Raman spectra can be registered down to 50 cm^{-1} , which means that crystals and lattice vibrations can be studied; also glass, quartz and other optical elements can be utilised. Further, by using NIR exciting radiation, especially the Nd:YAG (neodymium doped yttrium aluminium garnet) laser line at 1064 nm, the fluorescence can be minimized [14,15]. However, independent of these advantages ordinary Raman spectroscopy has not been applied until now for studying flotation processes. In one study [16], Raman spectra were used to differentiate between potassium amyl xanthate, lead amyl xanthate, and amyldixanthogen. Attempts to identify a collector reagent on the galena surface, however, have been unsuccessful. FT-Raman [17] and surface enhanced Raman spectroscopy (SERS) [18] were applied in a model investigation for characterization the ethyl xanthate compounds of potassium, sodium, copper, silver and gold on metal surfaces. It was concluded that Raman spectroscopy can be applied for distinguishing dioxanthogen and metal xanthates. From previous investigations on flotation of sulfide minerals it becomes apparent that examinations with using Raman spectroscopy have been mainly limited to studies on individual metal xanthates in model conditions.

In this paper, the Raman spectra of some surface products obtained by processing of chalcopyrite mineral with sodium isopropyl xanthate collector in model conditions and under conditions close to those employed in an industrial froth flotation are reported.

2. Experimental

The natural chalcopyrite (CuFeS_2) minerals were freshly ground just before conditioning with the collector. The flotation collector NaiPX, sodium isopropyl xanthate (Hoechst, Germany), technical grade, was purified by recrystallization before the experiments. Copper isopropyl xanthate-hydrate (CuIPX), iron isopropyl xanthate (FeiPX_3), and diisopropyldioxanthogen (iPX_2) were prepared according to procedures described elsewhere [5].

Two flotation experiments were performed: (i) a model study at high collector concentration of 50 g/l NaiPX water solution, and (ii) in conditions close to those employed in an industrial flotation—100 mg/l (5.7×10^{-4} mol/l) NaiPX water solution and 100 mg/l solution of a polyglycol-type frother reagent (DOW 250) in water. The freshly ground chalcopyrite minerals were conditioned for 10–15 min with the corresponding collector system (i) or (ii). The mineral surface was washed carefully with deionized water and the Raman spectra of the wet surface products were recorded. Raman spectra of the surface products were also registered before washing the conditioned mineral with deionised water.

The Raman measurements were performed using a dispersive Jobin Yvon T 64000 Raman spectrometer with a microprobe attachment. Excitation of the spectrometer was ensured by the 514.5 nm line of an argon ion laser with a power (at the laser outlet) 0.05–0.02 W, entrance slit 100 μm , 0.1–0.2 mm pinhole, 600 g/mm grating and measuring time between 1 and 20 min. The spectra were collected with a CCD detector using backscattering geometry and an objective lens with a X20 magnification. Raman spectra of the xanthates—solid reagents and water solutions as well as mineral–NaiPX reaction products—were registered between 60 and 4000 cm^{-1} , focusing the microscope above the mineral surface, in order to avoid sample heating.

The preliminary study on different xanthate homologues: sodium ethyl-, sodium *n*-propyl-, sodium *n*-butyl-, potassium amyl-, sodium isobutyl-xanthate, and NaiPX (Hoechst, Germany) pointed out that, except for NaiPX, the Raman spectra were almost completely masked by fluorescence from the collectors and/or the presence of impurities, even when the spectra were recorded immediately after recrystallization. Clearly this shows that dispersive Raman with argon ion laser excitation is not the proper choice of instrumentation for this purpose. The utilisation of an FT-Raman instrument would give better result [17], especially if a Nd:YAG laser excitation is used [14].

IR spectra of the individual compounds NaiPX, CuiPX, and iPX₂ were recorded on a Perkin–Elmer 1750 FTIR spectrophotometer in Nujol, perdeuterated Nujol mulls, and KBr pellets at 2 cm^{-1} resolution.

3. Results and discussion

The Raman spectra of NaiPX, CuiPX, and iPX₂ are shown in Figs. 1 and 2 and spectral data are collected in Table 1. Included in the Table 1 are also data from the registered IR spectra of the studied xanthates and the assignment of their bands based on the NaiPX ab initio force field treatment accomplished by Colthup and Powell [12].

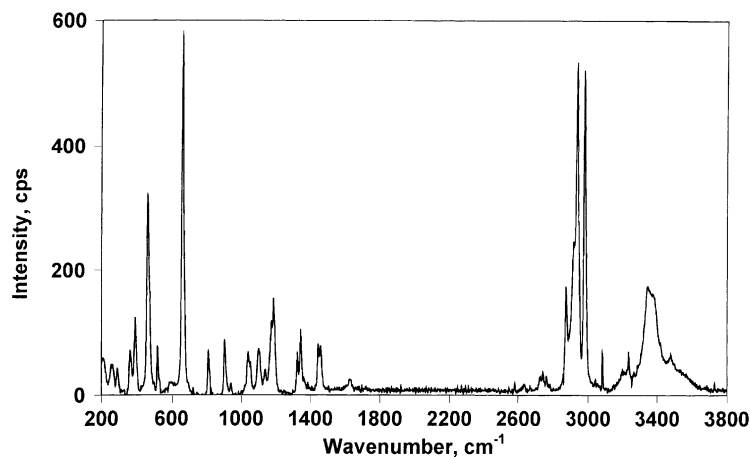


Fig. 1. Raman spectrum of solid sodium isopropyl xanthate-hydrate (NaiPX).

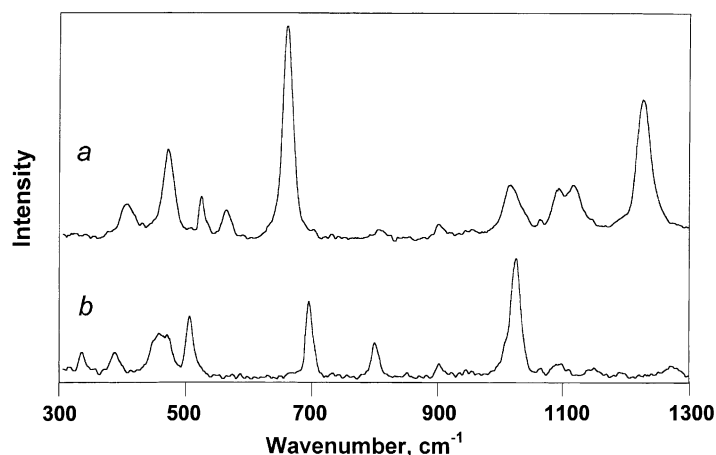


Fig. 2. Raman spectra of: line *a*—copper isopropyl xanthate (CuiPX); line *b*—diisopropyldixanthogen (iPX₂).

It is seen from the data in Table 1 that the CH stretching and bending vibrations do not change their positions in the studied xanthate molecules. FT Raman investigations of copper, silver and gold ethyl xanthates pointed out [17] that the metal–sulfur bond strengths are of the same order of magnitude as those in the alkali–xanthates. In agreement with these observations our data show that the SCS and COC vibrations do not change substantially their wavenumber positions in both NaiPX and CuiPX studied here (see Table 1). Nevertheless, the increase of the metal–sulfur bond strength in CuiPX compared to that of NaiPX is expected to provoke a decrease of the CS stretching frequencies and an increase of the CS bending frequencies due to the delocalisation of the electron density over S–Cu bonds. It is seen from the data in Table 1 that for CuiPX Raman spectrum $\nu_{as}(SCS)$ and $\nu_s(SCS)$ have about 30 and 4 cm^{-1} lower frequencies, respectively, whereas $\delta_{as}(SCS)$ shows 13 cm^{-1} higher frequency compared to those for NaiPX.

The $\nu(CS)$ double bond and $\nu(SS)$ single bond available in the iPX₂ molecule give rise to medium strong bands in the Raman spectrum of this compound at 694 and 502 cm^{-1} correspondingly (compare the spectra of CuiPX and iPX₂ in Fig. 2).

The data from the vibrational band assignment presented in Table 1 can be used for discriminating between CuiPX and iPX₂ when studying with Raman spectra the chalcopyrite–NaiPX flotation surface products.

3.1. Composition and structure of the surface products of the model system chalcopyrite–50 g/l NaiPX water solution

The collected surface products obtained during the interaction of chalcopyrite mineral with NaiPX were studied with Raman spectroscopy after rinsing the sample with water. The surface spectrum of unwashed 50 g/l NaiPX–chalcopyrite model system was also studied. The latter showed Raman bands that completely resemble the spectrum of the pure collector NaiPX probably because of its high concentration and eventual existence of precipitated NaiPX on the mineral surface.

When the mineral surface is carefully washed the precipitated species are expected to be removed. Indeed, after rinsing the samples, the registered Raman spectra of the remaining surface products did not contain NaiPX characteristic bands but a series of band maxima, which could be divided into two sets. The first set includes bands at the following wavenumbers: 1226/1217 s doublet, 1120 w, 1020 m, 910 w, 654 w, 275 w; and the second set—those at 1021 s, 797 w, 694 m, 502 w cm^{-1} (see Fig. 3a, Cpy-50 g/l NaiPX spectrum). The interpretation of both series of bands sets were made on the basis of comparative analyses with Raman bands of compounds possibly participating in the collection process on the chalcopyrite surface.

The IR investigations on sulfide minerals–xanthate surface products pointed out [10, 19 and

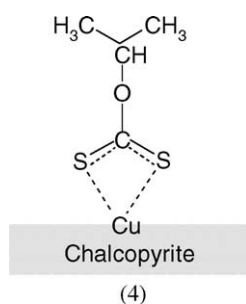
Table 1
Characteristic vibrational bands (cm^{-1}) registered for the studied xanthate compounds and their assignment

NaiPX		CuiPX		iPX ₂		Assignment ^a
Raman ^b	IR ^b	Raman ^b	IR ^b	Raman ^b	IR ^b	
3343 wbr	3382 sbr	–	–	–	–	$\nu(\text{OH})$
2977 s	2976 m	2979 m	2979 m	2984 s	2979 m	$\nu_{\text{as}}(\text{CH}_3)$
2935 s	2929 w	2933 w	2932 w	2935 s	2931 w	$\nu_{\text{as}}(\text{CH}_3)$
2917 m	–	–	–	–	–	$\nu(\text{CH})$
2871 m	2873 w	2867 w	2870 w	2871 wm	2870 w	$\nu_{\text{s}}(\text{CH}_3)$
1461 ms	1462 w	–	1462 w	1451 m	1467 m	$\delta_{\text{as}}(\text{CH}_3)$
1447 ms	1443 w	1445 m	1449 w	–	1450 m	$\delta_{\text{as}}(\text{CH}_3)$
–	1382	–	1382 w	–	1388 m	$\delta_{\text{s}}(\text{CH}_3)$
–	1373 m	–	1372 m	–	1374 m	$\delta_{\text{s}}(\text{CH}_3)$
1344 m	1338 w	1336 w	–	1351 wm	1353 m	$\omega(\text{CH})$
1326 m	1321 w	–	1266 s	–	–	$\omega(\text{CH})$
1189 m	1189 vs	1224 s	1226 vs	1271 w	1271 vs	$\nu_{\text{as}}(\text{COC})$
–	1140 s	–	1141 m	–	1146 m	$\rho_{\text{s}}(\text{CH}_3)$
1102 w	1090 vs	1094 m	1088 vs	1090 w	1083 s	$\nu_{\text{as}}(\text{CCC})$
1050 wm	1039 vs	1017 m	1011 vsbr	1024 vs	1028 s	$\nu_{\text{as}}(\text{SCS})$
–	–	–	1011 vsbr	–	1005 vs	$\nu_{\text{s}}(\text{COC})$
907 m	906 m	906 w	900 m	900 w	899 s	$\rho_{\text{as}}(\text{CH}_3)$
814 m	813 m	811 w	803 w	798 m	796 s	$\nu_{\text{s}}(\text{CCC})$
–	–	–	–	694 ms	691 w	$\nu(\text{C=S})$
663 vs	–	659 vs	–	–	–	$\nu_{\text{s}}(\text{SCS})$
–	576 w	562 m	561 w	–	567 w	$\omega(\text{SCS})$
508 w	509 m	523 w	526 w	–	–	$\delta_{\text{s}}(\text{CCC})$
–	–	–	–	502 ms	–	$\nu(\text{S-S})$
464 s	–	467 m	461 wm	453 mbr	–	$\delta_{\text{s}}(\text{COC})$
392 m	–	405 w	–	385 wm	–	$\delta_{\text{as}}(\text{SCS})$
363 m	–	–	–	334 wm	–	$\delta_{\text{as}}(\text{OCC})$
291 wm	–	–	–	–	–	$\delta_{\text{s}}(\text{SCS})$
–	–	275 w	–	–	–	$\rho(\text{SCS})$
203 wm	–	–	–	201 s	–	$\tau(\text{CH}_3)$

^a Vibrational modes: ν , stretching; δ , scissoring deformation; ρ , rocking; ω , wagging; τ , torsion; subscript s, symmetric; subscript as, antisymmetric.

^b Relative intensities: s, strong; vs, very strong; m, moderate; wm, weak to moderate; w, weak; br, broad.

references therein] that the copper atom is bonded to both sulfur atoms of the xanthate molecules—(4). The application of IR photo acoustic spectroscopy for



studying the interaction of ethyl xanthate with copper and chalcocite (Cu_2S) electrodes in certain conditions leads to the conclusion [10] for formation and degradation of diethyldixantogen (3).

Following the results of these IR studies we compared both sets of Raman bands obtained for the chalcocopyrite–NaiPX model system with the data for the individual compounds of CuiPX and iPX₂ depicted in Figs. 2 and 3. The comparison of the first set of spectrum bands with the data in Table 1 leads to the conclusion that these bands correspond to CuiPX. Therefore, the considered Raman spectrum bands confirm the existence of chemisorbed CuiPX

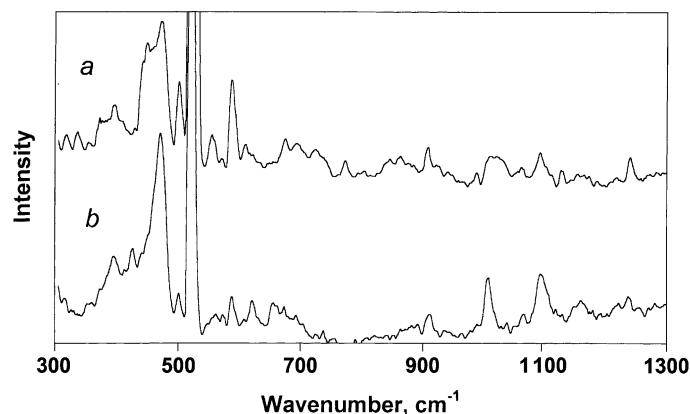


Fig. 3. Raman spectra of the surface product(s) obtained by processing of chalcopyrite with: *line a*—50 g/l NaiPX; *line b*—100 mg/l NaiPX and 100 mg/l frother DOW 250.

surface product obtained by conditioning the chalcopyrite with NaiPX. It must be noted here that, in principle, some deviation of the copper–isopropyl xanthate band positions could be expected for CuiPX–surface product (compared to the spectrum of CuiPX compound) as far as the copper atoms from the chalcopyrite surface are also connected with the sulfur and iron atoms from the crystal lattice. This could explain the splitting of the 1224 cm^{-1} band registered in the spectrum of the CuiPX individual compound which appear as a doublet $1226/1217\text{ cm}^{-1}$ in the Raman spectrum of chalcopyrite–NaiPX model system.

The second set of Raman bands resembles the $i\text{PX}_2$ spectrum bands position (see Figs. 2 and 3); only slight changes in the wavenumber are seen (compare also with Fig. 1 and the data in Table 1). It follows from these observations that the other surface product obtained after conditioning chalcopyrite with 50 g/l NaiPX water solution is $i\text{PX}_2$.

It is worth to stress again that the considered species, CuiPX and $i\text{PX}_2$, are obtained in the process of conditioning the chalcopyrite with 50 g/l NaiPX water solution. Raman spectra show that both products persist together on the crystal surface even after a thorough washing of the sample.

In their IR spectroscopic and electrochemical studies on the chain length influence of the xanthate collectors upon their adsorption on chalcopyrite, Mielczarski, et al. [7,8] have pointed out that, in

the case of ethyl xanthate, the first surface product is copper ethyl xanthate complex whereas, when amyl xanthate is used, the copper amyl xanthate is produced together with diamyldixanthogen. On the basis of these observations one can conclude that also in the model system studied here both species CuiPX and $i\text{PX}_2$ are formed together on the chalcopyrite surface. However, the results from the investigation of the flotation at much lower concentrations of the NaiPX given in Section 3.2 lead to the supposition that the first surface product by processing the chalcopyrite with NaiPX is CuiPX. Obviously the $i\text{PX}_2$ molecule could play also an important role in the flotation process, taking into account its remarkable ‘sticky’ properties being in a liquid state on the mineral surface at the working conditions.

3.2. Structure of the surface product of the flotation system chalcopyrite–100 mg/l NaiPX–100 mg/l frother

The processing of chalcopyrite minerals with a collecting system of 100 mg/l NaiPX–100 mg/l frother water solution corresponds to conditions near to those employed in an industrial flotation. Our study pointed out that the frother Raman bands at $855, 724, 692,$ and 675 cm^{-1} do not appear in the surface Raman spectrum registered after washing the minerals.

The Raman spectrum of the surface products on the chalcopyrite conditioned with this solution containing 100 mg/l of NaiPX and 100 mg/l frother, after washing, is presented in Fig. 3. The registered bands at 1226, 1094, 1010, 904, 655 and 469 cm^{-1} closely resemble those of the pure CuiPX; compare these wavenumbers with the data in Table 1. The results point out that the conditioning of chalcopyrite with NaiPX in concentration near to real flotation process favours the surface formation of the chemisorbed CuiPX. Spectral bands connected with iPX₂ were not detected, which could suggest that the eventual presence of iPX₂ at these working conditions is below the detection limit of the Raman spectroscopy.

From the spectra in Fig. 3 it is seen that the band intensities registered for both flotation systems, 100 mg/l NaiPX–100 mg/l frother and 50 g/l NaiPX are comparable; only the background of the former is lower.

The results from the last two points give a base for the assumption that by conditioning of chalcopyrite with NaiPX the first surface product is the chemisorbed CuiPX, probably followed by adsorption of iPX₂. As was mentioned above, both compounds are important for the successful flotation of the sulfide minerals.

3.3. Raman study of flotation concentrate

In order to test the potential of ordinary Raman spectroscopy for studying the surface flotation

products, we attempted to register the Raman spectrum of a real flotation concentrate. The latter has been obtained after a preliminary treatment of the feed material with 10 mg/l Fe³⁺ solution and then floated with 41 mg/l NaiPX (2.5×10^{-4} mol/l), washed, dried and stored for several days. The registered Raman spectrum depicted in Fig. 4 shows bands at the following wavenumber positions: 1237, 1093, 908, 880, 670, 724, 610, 585, 441 cm^{-1} .

In Fig. 4b is also given the Raman spectrum of FeiPX₃. We have assigned the registered FeiPX₃ bands by analogy to the data in Table 1 as follows: 1260 w— $\nu_{\text{as}}(\text{COC})$, 1104 wm— $\nu_{\text{as}}(\text{CCC})$, 1062 ms— $\nu_{\text{as}}(\text{SCS})$, 884mbr— $\rho_{\text{as}}(\text{SCS})$, 663 s— $\delta_{\text{s}}(\text{SCS})$, 471 ms— $\delta_{\text{as}}(\text{COC})$, 391mbr— $\delta_{\text{as}}(\text{SCS})$, 308 s— $\delta_{\text{s}}(\text{SCS})$. The comparison of these bands with the Raman spectrum of the flotation concentrate leads to the assumption that FeiPX₃ is one of the products present on the chalcopyrite surface. This is perhaps related to the modification of the mineral surface with Fe³⁺ and its preferable interaction with the collector. However, the registered band at 1237 cm^{-1} is shifted downwards from the $\nu(\text{C-O-C})$ band of FeiPX₃ (1260 cm^{-1}). This could be explained with the complexation of Fe³⁺ not only with the CS₂ group of the isopropyl xanthate but also with the other oxygen atom of the C-O-S group leading to a decrease of the characteristic band frequency from 1260 cm^{-1} .

Finally, the detected surface product on the flotation concentrate by means of Raman

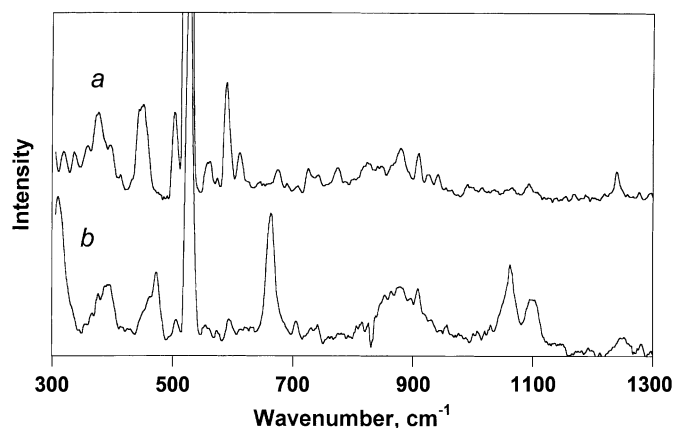


Fig. 4. Raman spectra of: line *a*—the surface products obtained by pre-treatment of the feed material with 10 mg/l Fe³⁺ then floated with 41 mg/l NaiPX, washed, dried and stored for several days; line *b*—iron isopropyl xanthate (FeiPX₃).

spectroscopy is of interest as other workers have indicated that the surface products appear to be unstable [10,20]. Therefore, Raman spectroscopy will be a useful tool in further investigations to determine the composition and structure of the molecular species responsible for the flotation behaviour.

4. Conclusion

Two reaction products were determined with Raman spectroscopy to be present on the chalcopyrite surface when performing flotation at high Na₂PX collector concentration: the chemisorbed Cu₂PX and the physically adsorbed iPX₂. When the reaction process is carried out in conditions near to real industrial froth flotation, Cu₂PX was the only product found on the chalcopyrite surface; measurable quantity of iPX₂ was not detected. Raman spectroscopy gives evidence to suppose that Fe₂PX₃ is present as a surface product on a real flotation concentrate, dried and stored for several days, and obtained from a feed material preliminary treated with Fe³⁺ solution.

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