

Article

## The Interaction Between Titanium(IV) and the Croconate Ion in Aqueous Solution Studied by Resonance Raman Spectroscopy

Lucia Kiyomi Noda, Norberto Sanches Gonçalves<sup>a\*</sup>,

Paulo Sergio Santos and Oswaldo Sala

Laboratório de Espectroscopia Molecular, Instituto de Química da Universidade de São Paulo, CP 26077, 05599-970 São Paulo - SP, Brazil

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Neste trabalho, a interação entre o íon Ti(IV) e o oxocarbono croconato em solução aquosa foi investigada através da espectroscopia Raman ressonante. O complexo formado possui uma coloração alaranjada intensa atribuída à presença de uma banda de transferência de carga em torno de 400 nm. Os perfis de excitação Raman do complexo mostram um padrão de intensificação para os modos totalmente simétricos substancialmente distinto do usual para os oxocarbonos livres. Os modos mais significativamente afetados pela coordenação são aqueles envolvendo os grupos carbonílicos, exibindo apreciáveis desdobramentos e deslocamentos de frequência. Isto indica que a interação é bastante accentuada, envolvendo provavelmente as carbonilas do anel oxocarbônico.

In this work, a resonance Raman investigation was undertaken in order to elucidate the interaction between Ti(IV) and the croconate ion in aqueous solution. The intense orange-red color characteristic of the complex was assigned to a charge transfer transition around 400 nm. The Raman excitation profiles of the complex show an intensification pattern for the totally symmetric modes that is unusual for free oxocarbons. The modes involving the carbonyl groups are the most affected by coordination, exhibiting substantial shifts and splittings, which indicate that the interaction is quite strong, probably involving the oxocarbon carbonylic moieties.

**Keywords:** croconate, titanium(IV), resonance Raman spectroscopy

### Introduction

Oxocarbon ions are cyclic species of the general formula  $C_nO_n^{2-}$ , which from the point of view of Raman spectroscopy are notable for their unusual pattern of enhancement involving non-totally symmetric modes<sup>1,2</sup>. Such behavior has been attributed to the Jahn-Teller effect in the first allowed excited state of these species, and in this respect Raman spectroscopy has been instrumental in providing firm evidence<sup>3</sup>.

On the other hand, Oxocarbons, and in particular the croconate ion  $C_5O_5^{2-}$ , have shown to be versatile ligands for transition metal ions, with several of their coordination compounds characterized mainly by X-ray crystallography<sup>4,5</sup>, magnetic susceptibility/EPR<sup>6</sup>, and vibrational spectroscopy<sup>7,8</sup>. Of particular interest in this context is the question related to the aforementioned unusual pattern of the isolated oxocarbon when coordinated to transition met-

al ions. In several coordination species involving oxocarbons as croconate and squarate ( $C_4O_4^{2-}$ ), the enhancement pattern is very similar to that observed for the free oxocarbon ions<sup>9</sup>. In the course of extending such investigations to "earlier" transition metals in high oxidation states, we have investigated the interaction of croconate with Ti(IV) in acidic media, which gives rise to intense orange-red solutions. The study of such a system by means of optical and resonance Raman spectroscopy led us to conclude that a strong charge-transfer interaction between croconate and Ti(IV) is present, as revealed by a drastic modification in the enhancement pattern of the croconate modes, as well as by the outstanding splitting of degenerate ones. Such observations are in sharp contrast to previous ones on coordination species of oxocarbon, and indicate that in the present case the enhancement mechanism involves the pre-resonance contribution of the internal transition of croconate,

<sup>a</sup> permanent address: Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis - SC, Brazil.

as well as a marked resonance contribution of the charge transfer transition.

Although the exact nature of the species present in titanyl sulfate aqueous solutions is still controversial (the "titanyl" question<sup>10</sup>), we will refer to it simply as Ti(IV).

## Experimental

The Ti(IV) stock solution was prepared by the dissolution of 5.0 g of titanium oxysulfate sulfuric acid complex ( $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot y\text{H}_2\text{O}$ , ALDRICH) in the minimum amount of concentrated sulfuric acid (MERCK), under heating and stirring. After the dissolution, the remaining colloidal  $\text{TiO}_2$  was removed by filtration in a sinterized glass funnel. After cooling, this solution was placed in a 100 mL volumetric flask and filled with deionized water. The Ti(IV) concentration was determined gravimetrically to be ca.  $0.95 \text{ mol L}^{-1}$ , and the sulfuric acid as roughly  $2.0 \text{ mol L}^{-1}$ . Lithium croconate dihydrate was prepared with minor modifications according to the method reported by Fatiadi<sup>11</sup>. The concentration ratio between Ti(IV) and croconate which represents the best compromise between absorbance, Raman intensity and stability, was found to be  $5 \times 10^{-3} \text{ mol L}^{-1}$  in croconate and  $5 \times 10^{-2} \text{ mol L}^{-1}$  in titanium (IV), with a pH value around 1. We also observed that at lower pH values the complex photolability increases, probably due to displacement of the equilibrium towards

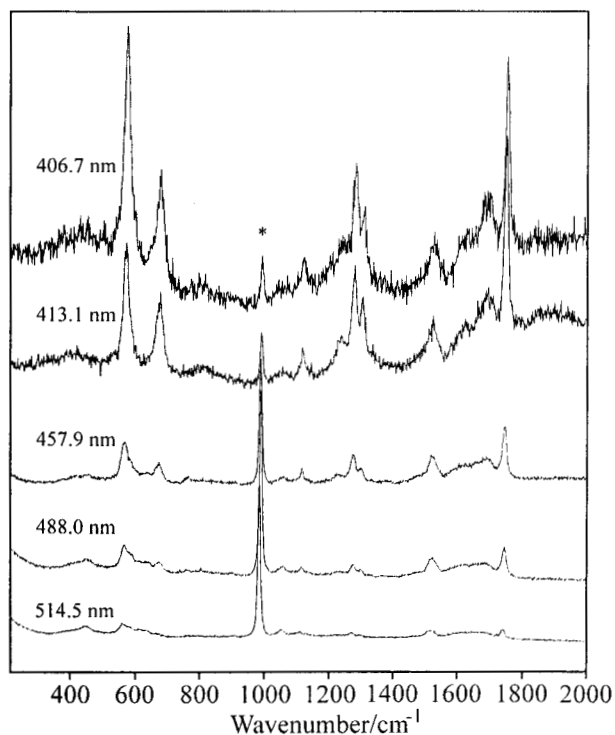
the formation of the croconic acid (according to Carlqvist and Dyrssen<sup>12</sup>,  $\text{p}K_1 = 0.5$  and  $\text{p}K_2 = 2.0$ ), which is known to be photolabile<sup>13,14</sup>. On the other side, higher pH values led to Ti(IV) hydrolysis. As a Raman internal standard,  $1.0 \text{ mol L}^{-1}$  lithium sulfate hydrate was added.

In order to compare the intensification pattern, we also obtained the Raman excitation profiles for the free croconate, by using a  $10^{-2} \text{ mol L}^{-1}$  solution in croconate and  $1.0 \text{ mol L}^{-1}$  in potassium nitrate (as the internal standard).

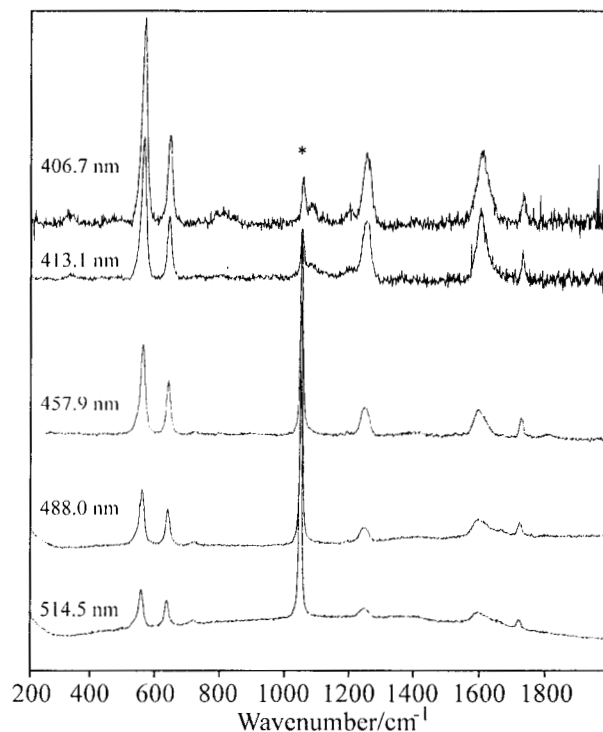
The Raman spectra of the croconate at different pH values (1, 2 and 7) were also obtained in order to evaluate the effect of protonating the ligand itself. The solutions were  $5 \times 10^{-3} \text{ mol L}^{-1}$  in croconate and at lower pH values sulfuric acid was employed. The spectra agree well with previously reported data<sup>12</sup>.

Raman spectra were obtained in a Jobin-Yvon U-1000 spectrometer fitted with a RCA C31034A-02 photomultiplier tube and photon counting electronics (EG&G PARC). A personal computer was used to control the spectrometer and acquire the data by means of PRISM software. Laser excitation was provided by two Coherent Innova (90-6,  $\text{Ar}^+$  and 90K,  $\text{Kr}^+$ ), with 514.5, 488.0, 457.9, 413.1 and 406.7 nm lines, with power ranging from 100 to 200 mW. The sample was placed in a rotatory cell, and the scattered radiation was passed through a scrambler.

Optical spectra were obtained using plane capillary cells (0.01 mm) in a Beckman DU-70.



**Figure 1.** Raman spectra of the  $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$   $5 \times 10^{-3} \text{ mol L}^{-1}$  / Ti(IV)  $5 \times 10^{-2} \text{ mol L}^{-1}$  /  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$   $1.0 \text{ mol L}^{-1}$  aqueous solution excited by the indicated radiations. Spectral resolution =  $7 \text{ cm}^{-1}$ . \*Band of the internal standard, sulfate ion.



**Figure 2.** Raman spectra of the  $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$   $10^{-2} \text{ mol L}^{-1}$  /  $\text{KNO}_3$   $1.0 \text{ mol L}^{-1}$  aqueous solution excited by the indicated radiations. Spectral resolution =  $7 \text{ cm}^{-1}$ . \*Band of the internal standard, nitrate ion.

Spectral data were analyzed using the Grams package (Galactic Industries). The Raman spectra were deconvolved by using mixed Gaussian-Lorentzian fitting functions. Raman excitation profiles were then built-up by using peak heights taken from the resulting fittings, and normalized in relation to the 514.5 nm excitation line, which permits the evaluation of the intensification factor for each specific normal mode.

## Results and Discussion

The Raman spectra of the complex and the free croconate solutions excited by several laser lines are displayed in Figs. 1 and 2, respectively. The Raman spectra of the croconate ion at different pH values are shown in Fig. 3. The corresponding Raman shifts are listed in Table 1 with a tentative assignment.

The optical absorption spectra of the complex solution, the croconate ion at several pH values, and Ti(IV) in acidic solution are displayed in Fig. 4.

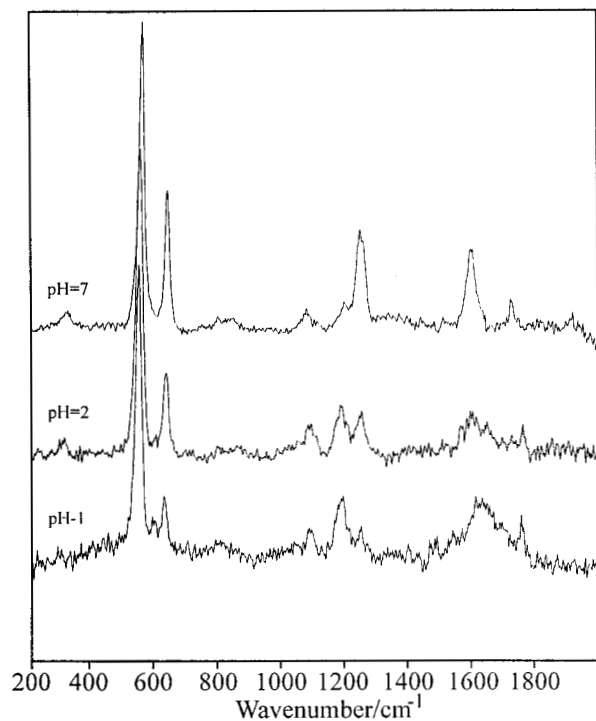
The normalized excitation profiles of the most prominent bands of the complex superposed on its optical absorption spectrum are shown in Fig. 5. For the purposes of comparison the corresponding data for free croconate are also shown in Fig. 6, together with its optical absorption spectrum at a neutral pH.

The analysis of Figs. 1 and 2 shows several drastic changes in the Raman spectrum of the croconate moiety in the croconate/Ti(IV) system. In particular, the degenerated modes  $\nu_{10}$  and  $\nu_9$  show up as split bands. In addition, there is an appreciable shift in several modes. These observations indicate that a strong interaction takes place. Another point worth mentioning is the unusual enhancement (for the

**Table 1.** Vibrational frequencies ( $\text{cm}^{-1}$ ) and tentative assignment\* for the croconate ion and its Ti(IV) complex in aqueous solution.

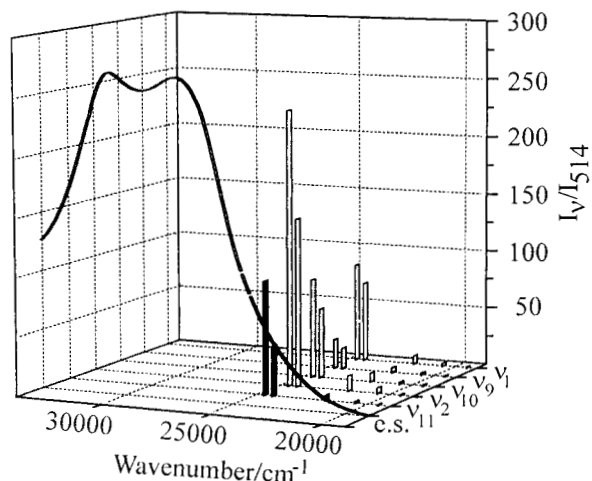
free croc.**	$\nu$ ( $\text{cm}^{-1}$ )		sym. ( $D_{5h}$ ) activity			assignment
	pH = 2	complex***				
248(s)			$a''_2$	IR	$\nu_4$	o.p.C=O bending
329(w)	319(w)	411(w)	$e''_1$	R(dp)	$\nu_8$	o.p.C=O bending
374(m)			$e'_1$	IR	$\nu_7$	i.p.C=O bending
530(sh)			$e'_2$	R(dp)	$\nu_{12}$	i.p.C=O bending
558(vs,dp)	552(vs)	567(s)	$e'_2$	R(dp)	$\nu_{11}$	ring bending
637(m,p)	635(m)	675(m)	$a'_1$	R(p)	$\nu_2$	ring breathing
		760(w)				
		1053(w)				$\text{HSO}_4^-$
1100(w)			$e'_1$	IR	$\nu_6$	C-C stretching
1074(w)	1090(w)	1112(w)				$2 \nu_{11}$
1193(w)	1182(w)	1220(w)				$\nu_{11} + \nu_2$
1245(m,dp)	1249(m)	1272(m)	$e'_2$	R(dp)	$\nu_{10}$	C-C stretching
		1297(m)				
		1373(vw)	$a'_2$	inactive	$\nu_3$	i.p.C=O bending
		1465(vw)				
1570(vs,vbr)			$e'_1$	IR	$\nu_5$	C=O stretching
1594(m,dp)	1598(m)	1517(s)	$e'_2$	R(dp)	$\nu_9$	C=O stretching
		1617(m)				
		1690(m)				
1722(w,p)	1756(w)	1740(vs)	$a'_1$	R(p)	$\nu_1$	sym. C=O stretching
			$e''_2$	inactive	$\nu_{13}$	ring twisting
			$e''_2$	inactive	$\nu_{14}$	o.p.C=O bending

\* based on the work of Ito and West, Ref. 14; \*\* relative Raman intensities for 406.7 nm excitation; \*\*\* relative Raman intensities for 488.0 nm excitation; vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad, p = polarized, dp = depolarized, i.p.= in plane, o.p.=out of plane, sym = symmetric, R = Raman and IR = infrared.

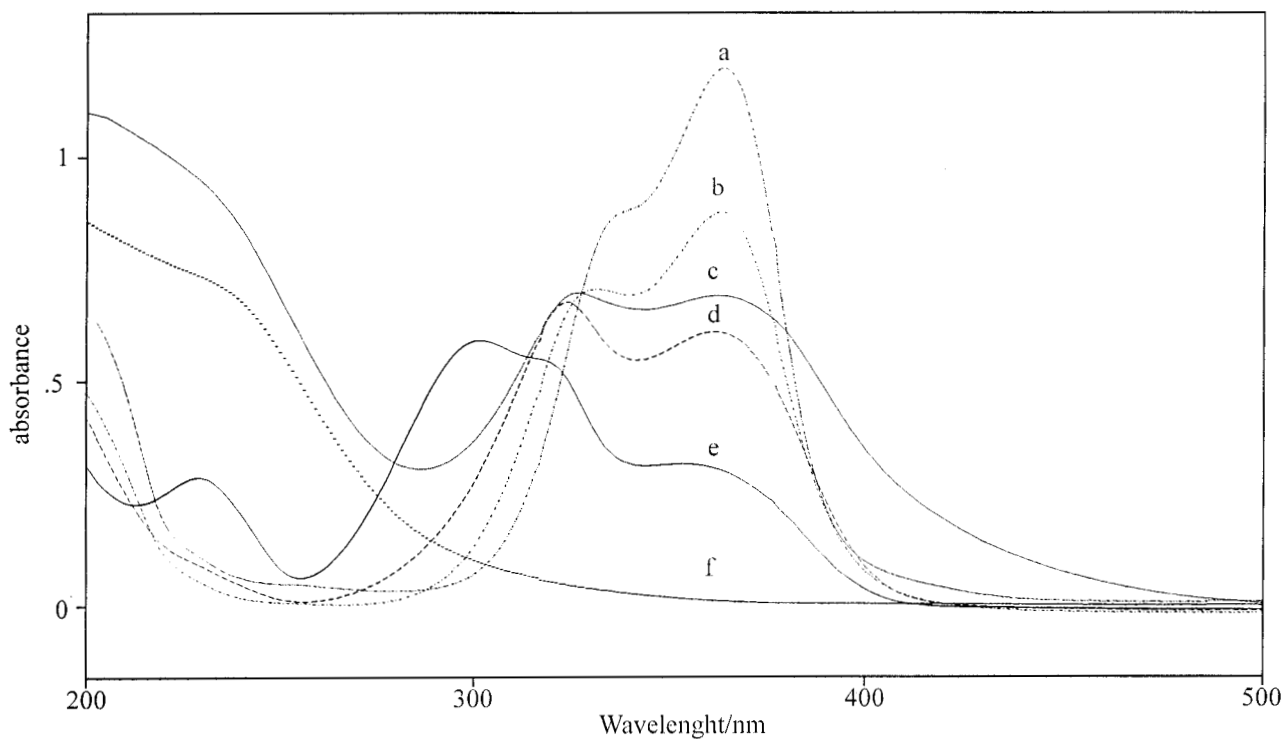


**Figure 3.** Raman spectra of the  $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$   $5 \times 10^{-3} \text{ mol L}^{-1}$  aqueous solutions at the indicated pH's. Excitation: 406.7 nm.

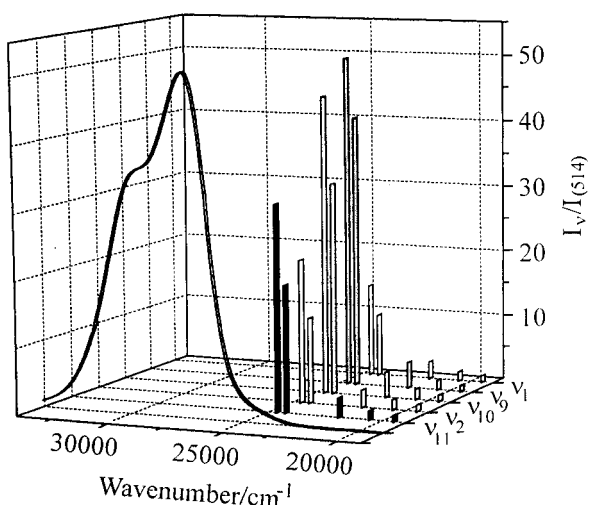
oxocarbons) and frequency shifts of the totally symmetric modes  $\nu_1$  (carbonyl stretching mode, *ca.*  $1740 \text{ cm}^{-1}$ ) and  $\nu_2$  (ring breathing, *ca.*  $676 \text{ cm}^{-1}$ ). In fact, the  $\nu_1$  mode in the free oxocarbons is amongst the weaker ones. The changes mentioned before cannot be assigned to the presence of



**Figure 5.** Raman excitation profiles of the indicated vibrational modes of the Ti(IV)/croconate complex superimposed on the optical absorption spectrum of the  $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$   $5 \times 10^{-3} \text{ mol L}^{-1}$  / Ti(IV)  $5 \times 10^{-2} \text{ mol L}^{-1}$  aqueous solution. Each profile is normalized to 514.5 nm excitation.



**Figure 4.** Optical absorption spectra of the indicated aqueous solutions: a) croconate  $5 \times 10^{-3} \text{ mol L}^{-1}$ , pH=7; b) croconate  $5 \times 10^{-3} \text{ mol L}^{-1}$ , pH=2; c) croconate  $5 \times 10^{-3} \text{ mol L}^{-1}$ /Ti(IV)  $5 \times 10^{-2} \text{ mol L}^{-1}$ , pH=1; d) croconate  $5 \times 10^{-3} \text{ mol L}^{-1}$ , pH=1; e) croconate  $5 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{H}^+]=2 \text{ mol L}^{-1}$ ; f) Ti(IV)  $5 \times 10^{-2} \text{ mol L}^{-1}$ . Optical path=0.01 mm.

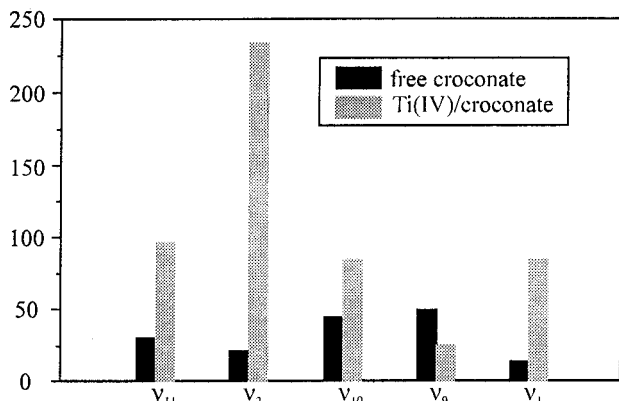


**Figure 6.** Raman excitation profiles (normalized to 514.5 nm excitation) of the indicated vibrational modes of free croconate superimposed on its optical absorption spectrum.

protonated or unprotonated forms of croconate ion, as can be seen in Fig. 3.

From the Raman excitation profiles, displayed in Figs. 5 and 6, it is obvious that in the croconate/Ti(IV) system the totally symmetric modes,  $\nu_1$  and  $\nu_2$ , present a noticeable enhancement compared to the free croconate. In order to illustrate such a change in the behavior of the enhancement factors, compared to the free croconate, Fig. 7 shows the normalized enhanced factors for several vibrational modes of free and coordinated croconate and the ratio of the complex and free croconate factors, confirming the above considerations.

From the optical spectrum, it is not possible to directly observe the charge transfer band, due to the overlapping with the strong absorption of the free croconate remaining in solution, although the evident broadening of the wing at the red side indicate the presence of a new feature. In fact,



**Figure 7.** The ordinate scale represents the normalized enhancement factors for several modes of free and coordinated croconate. The numbers at the top of the bars represent the ratio of such enhancement factors between these two species.

this point is clarified by inspection of Fig. 4 (c), where it is possible to see the absorption spectrum of the complex, together with the optical spectra of the croconate at several pH values (a, b, d and e). The optical spectrum of the Ti(IV) ion is also shown (Fig. 4f) for the purposes of comparison. It is evident that neither the free croconate species (protonated or unprotonated), nor the Ti(IV) ion itself, present this remarkable broadening at the high wavelength side. Also, from the profiles in Fig. 5 it is evident that a band component around 400 nm should be present in order to justify the enormous Raman enhancement from 488.0 to 406.7 nm. From the peculiar enhancement of the carbonyl symmetric stretching mode ( $\nu_1$ ), it is very likely that such a band is of the charge transfer nature, involving the interaction of the carbonylic moiety of the oxocarbon with the rather strong electron acceptor represented by the Ti(IV) species in solution.

This seems to be the first firm evidence of a substantial charge transfer interaction involving an oxocarbon with a transition metal species, reverting the enhancement pattern observed for free oxocarbons. At the moment, other oxocarbons such as squarate, are being investigated in order to better understand this interaction with Ti(IV).

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