

# Pre-resonant Raman effect of $\text{CrO}_4^{2-}$ in a metasilicate glass

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Received 16 November 1993; revised 22 June 1995

## Abstract

Pre-resonant Raman effect of chromate ion,  $\text{CrO}_4^{2-}$ , was observed in a metasilicate glass with molar composition  $2\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 3\text{SiO}_2$  containing 1.0 wt% of  $\text{Cr}_2\text{O}_3$ . Raman spectra were measured by the conventional  $90^\circ$  scattering geometry and by the microprobe Raman spectroscopic techniques. The presence of chromate ions in the glass is favoured by the glass composition and oxidizing conditions during the glass melting, and they are responsible for optical absorption bands at 370 and 250 nm. Raman spectrum of the undoped glass presents bands at 625, 860 and  $980\text{ cm}^{-1}$ , and the presence of chromate ions gives rise to additional bands at 365, 850 and a shoulder at  $890\text{ cm}^{-1}$ . An enhancement of the  $850\text{ cm}^{-1}$  Raman band is observed with decreasing laser exciting wavelength. The exciting frequency dependence of the intensity of this band is discussed in terms of theoretical models given in the literature.

## 1. Introduction

The resonant Raman effect consists of an anomalous increase in the intensity of the scattered radiation, as the exciting radiation frequency equals the absorption frequency of a molecule [1]. The pre-resonant Raman effect occurs when the virtual state in the Raman transition coincides with lower energy levels of allowed electronic transitions in the molecule, and the scattered radiation has a lower intensity than in the resonant case [1].

The anomalous increase of the scattered radiation intensity,  $I_s$ , with the exciting frequency,  $\tilde{\nu}_i = \lambda_i^{-1}$ , is due to the dependence of the Raman scattering tensor with this frequency. This dependence causes a deviation of the fourth power law,  $I_s \propto \tilde{\nu}_i^4$ , for the scattered radiation intensity [1].

Based on early theories, Albrecht and Hutley [2] analyzed the experimental intensity dependence of the  $1334\text{ cm}^{-1}$  Raman band of *p*-nitroaniline, dissolved in benzene [3], with the exciting frequency when one or two electronic transitions are involved. They used the adimensional factors  $F_A^2$  and  $F_B^2$ :

$$I_s \propto F_A^2 = \left[ \frac{\tilde{\nu}_s^2 (\tilde{\nu}_e^2 + \tilde{\nu}_i^2)}{(\tilde{\nu}_e^2 - \tilde{\nu}_i^2)^2} \right]^2, \quad (1)$$

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and

$$I_s \propto F_B^2 = \left[ \frac{2\tilde{\nu}_s^2 (\tilde{\nu}_e \tilde{\nu}_f + \tilde{\nu}_i^2)}{(\tilde{\nu}_e^2 - \tilde{\nu}_i^2)(\tilde{\nu}_f^2 - \tilde{\nu}_i^2)} \right]^2, \quad (2)$$

where  $\tilde{\nu}_s = \tilde{\nu}_i - \tilde{\nu}_m$  ( $\tilde{\nu}_m$  is the frequency of the Raman band which undergoes the anomalous increase of intensity), and  $\tilde{\nu}_e$  and  $\tilde{\nu}_f$  are the electronic transition frequencies. Eq. (2) was found to give the best fit for pre-resonant effect in *p*-nitroaniline [2].

The resonant Raman effect was observed for many coloured solutions of organic substances [4,5]. Doing and Prendergast [6] measured the pre-resonant spectra of a solution of tryptophan and phenylalanine with ultraviolet exciting wavelength using a continuously tunable, quasi-continuous-wave laser source.

For inorganic substances, the effect is less common. Kiefer and Bernstein [7] measured the resonant Raman effect of  $\text{MnO}_4^{2-}$  ions in aqueous solutions and in  $\text{KMnO}_4$  crystals, and of  $\text{I}_3^-$  (triiodide) ions dissolved in a solution of  $\text{CHCl}_2$  and  $\text{CS}_2$ . The resonant effect was recently measured for uranyl nitrate dissolved in dimethyl sulfoxide [8]. The effect was also observed for molecules adsorbed on metal surfaces [9,10], superlattices [11], intrinsic germanium surfaces [12] and  $\text{CdS}_x\text{Se}_{1-x}$  semiconductor microcrystals in glasses [13].

Raman spectra of chromate ions,  $\text{CrO}_4^{2-}$ , in aqueous solutions and in solid state were first measured by Venkateswaran [14], who identified the Raman bands and the corresponding vibrational modes, characteristic of tetrahedral molecules ( $T_d$  symmetry). Stammreich et al. [15] performed Raman measurements to correct the frequencies of the bands and re-evaluated the force constants for each vibrational mode of the chromate ion and the modes resulting from the interactions between the fundamental ones. Subsequent publications [16,17] confirmed these Raman frequencies and the corresponding vibrational modes, which are reported in Table 1.

Kiefer and Bernstein [18] presented pre-resonant and resonant Raman spectra of  $\text{CrO}_4^{2-}$  in solution and in  $\text{K}_2\text{CrO}_4$  crystalline powder and confirmed the validity of Eq. (2) for the  $850\text{ cm}^{-1}$  Raman band which suffers change in intensity with the incident radiation frequency. They used the absorption spec-

Table 1

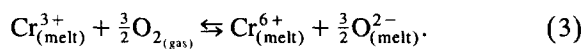
Frequencies and assignments of Raman bands of chromate ions,  $\text{CrO}_4^{2-}$ , in aqueous solution, after Ref. [17]. The values in parentheses are the percentual relative intensities of the bands, and 'p' and 'dp' mean that the bands are completely polarized or depolarized, respectively

$\tilde{\nu}_m$ ( $\text{cm}^{-1}$ )	Vibrational mode
348(27) dp	$\nu_2$ (E): symmetric bending
371(19) dp	$\nu_4$ ( $F_2$ ): asymmetric bending
846(100) p	$\nu_1$ ( $A_1$ ): symmetric stretching
887(21) dp	$\nu_3$ ( $F_2$ ): asymmetric stretching

tra obtained by Johnson and McGlynn [19]:  $\tilde{\nu}_e = 26\,900\text{ cm}^{-1}$  ( $\lambda_e = 370\text{ nm}$ ),  $\tilde{\nu}_f = 36\,600\text{ cm}^{-1}$  ( $\lambda_f = 275\text{ nm}$ ).

Raman spectra of oxide glasses containing  $\text{CrO}_4^{2-}$  were measured by Brawer and White [20] and Nelson et al. [21]. They concluded that the dissolved chromate ions are isolated in the glass matrix, since the Raman spectra of these ions, both in glasses and in aqueous solutions, are essentially the same in terms of band frequency, width and polarization. However, they made no consideration about the possibility of the observed pre-resonant Raman effect of the ion in glasses.

According to Nath and Douglas [22], during the melting in air of soda-silica glasses doped with  $\text{Cr}_2\text{O}_3$ , the following  $\text{Cr}^{3+} - \text{Cr}^{6+}$  equilibrium reaction takes place:



This reaction shifts to the right with the increase of alkali content in the melt.

The high concentration of modifier oxides in the  $2\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 3\text{SiO}_2$  metasilicate glass and its melting in air are sufficient conditions to promote the oxidation of a considerable number of  $\text{Cr}^{3+}$  ions to  $\text{Cr}^{6+}$  ions, according to Eq. (3), in the form of  $\text{CrO}_4^{2-}$  molecular ions.

In the present work, the pre-resonant Raman effect due to  $\text{CrO}_4^{2-}$  ions in the  $2\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 3\text{SiO}_2$  glass is reported, and the dependence of the intensity of the  $850\text{ cm}^{-1}$  Raman band with the exciting wavelength is analyzed through Eqs. (1) and (2). Raman spectra were obtained using the conventional

90° scattering geometry and the microprobe technique.

## 2. Experimental

Appropriate quantities of reagent-grade sodium and calcium carbonates (Riedel deHaën, and Merck, respectively), quartz sand (Mineração Jundu) and 1.0 wt% Cr<sub>2</sub>O<sub>3</sub> (Merck) were melted in a platinum crucible in a Global furnace at 1350°C in air. The melt was homogenized during 1 h with a platinum stirrer, cast on an iron plate and pressed with a stainless steel disc. The cooling rate was higher than 400°C/min, fast enough to prevent glass crystallization. The final glass was transparent, green and without visible bubbles, striae or crystallites.

For measuring the Raman spectra at the 90° scattering geometry, the faces of a sample with dimensions about (3 × 4 × 5) mm<sup>3</sup> were polished to an optical degree with an aqueous slurry of cerium oxide (1.0 μm) on a pitch tool. A sample with one partially polished surface was prepared for micro-Raman measurements.

The 90° scattering geometry Raman spectra were measured using an argon (Ar) laser (2020 Spectra Physics), a double diffraction grating spectrometer (1402 Spex) and a water cooled photomultiplier (C31034-RF Products for Research). The data were computer processed. Unpolarized spectra were measured with a resolution of about 1 cm<sup>-1</sup>. The sample was positioned so that the exciting laser beam was as near as possible to the surface of the output scattered radiation. This surface was parallel to the entrance slit of the spectrometer. Such procedure was taken to minimize the absorption of the scattered radiation inside the sample.

Raman microprobe spectra of the sample surface were obtained employing a triple monochromator Micro-Raman System (XY Dilor) equipped with a multichannel detector (Gold array-detector). The sample was also excited with an Ar laser (Innova 70-2, Coherent), with output power of about 700 mW for the 514.5 and 488.0 nm laser lines and 150 mW for the 457.9 nm line.

For optical absorption spectra measurements near the ultraviolet region, a glass with the same composition and with about 0.1 wt% of Cr<sub>2</sub>O<sub>3</sub> was prepared

using the same protocol. The final glass presents the same visual characteristics as the first one, except it is light yellow–greenish in colour.

Optical absorption spectra were measured with a double beam spectrometer (Cary 17 Varian).

All measurements were performed at room temperature.

## 3. Results

The optical density spectra,  $OD = \log_{10}(I_0/I)$  [23], of the glasses are shown in Fig. 1, together with the location of the Ar laser lines. The inset shows the absorption bands of the chromate ion at 370 and about 250 nm. The band centered at 650 nm is due to electronic transitions involving the ground state, <sup>2</sup>A<sub>4</sub>, and the excited state, <sup>4</sup>T<sub>2</sub>, of the Cr<sup>3+</sup>. Dips appear at 650 and 680 nm due to Fano anti-resonance effect, involving the forbidden levels, <sup>2</sup>T<sub>1</sub> and <sup>2</sup>E, respectively [24].

Fig. 2 shows the Raman spectra (90° scattering geometry) of the undoped and Cr<sub>2</sub>O<sub>3</sub> doped glasses, using the 488.0 nm laser line. No data reduction [25] was made since, in the case of the doped glass, it is very difficult to determine the temperature in the optical path of the laser beam inside the sample.

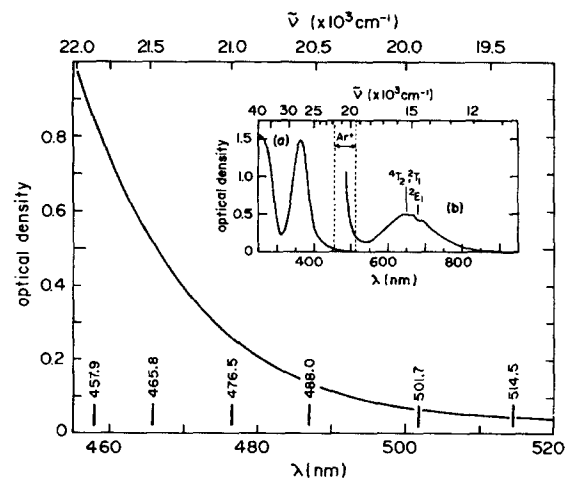


Fig. 1. Absorption spectrum of the glass with 1.0 wt% Cr<sub>2</sub>O<sub>3</sub> (thickness: 0.40 mm) in the range of the Ar laser lines. Inset: absorption spectrum of (a) the glass with about 0.1 wt% Cr<sub>2</sub>O<sub>3</sub> (thickness: 0.25 mm), and (b) the glass with 1.0 wt% Cr<sub>2</sub>O<sub>3</sub> (thickness: 2.88 mm).

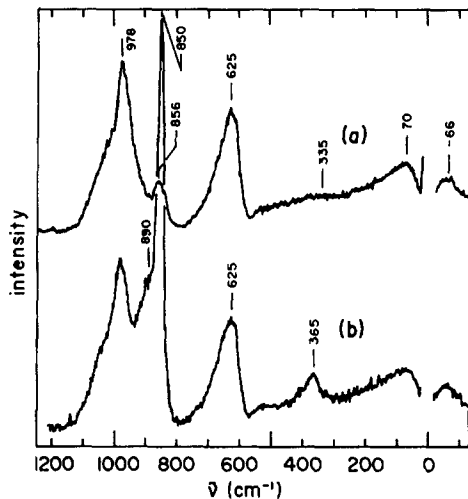


Fig. 2. Raman spectra ( $90^\circ$  scattering geometry) of the  $2\text{Na}_2\text{O}\cdot\text{CaO}\cdot 3\text{SiO}_2$  glass samples: (a) undoped and (b) doped with 1.0 wt%  $\text{Cr}_2\text{O}_3$  ( $\lambda_i = 488$  nm, laser power:  $\approx 500$  mW).

Moreover, the data reduction is an important procedure when the low frequency range of the spectrum of amorphous materials is analyzed [26].

The Raman spectrum (a), in Fig. 2, of the undoped glass presents intense bands at  $625$  and  $978$   $\text{cm}^{-1}$ . The band at  $625$   $\text{cm}^{-1}$  has an asymmetric shape and is attributed to superimposed symmetric and asymmetric bending vibration of  $\text{O}^-$ -Si- $\text{O}^-$  bonds [27]. The band at  $978$   $\text{cm}^{-1}$  is a superposition

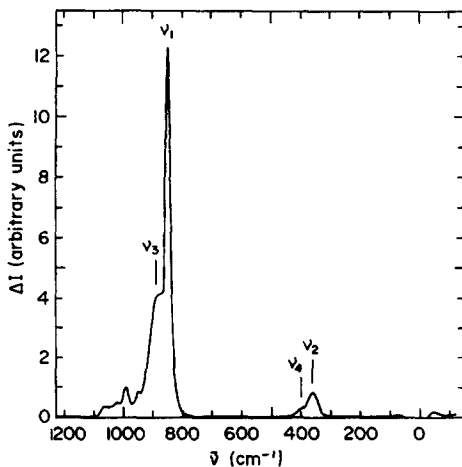


Fig. 3. Result of the subtraction of the undoped glass from the  $\text{Cr}_2\text{O}_3$  doped glass Raman spectra of Fig. 2 after intensity normalization of the spectra with respect to the band at  $625$   $\text{cm}^{-1}$ .

of symmetric stretching of  $\text{SiO}_4$  tetrahedra with one, two and three non-bridging oxygens (NBO), and the  $856$   $\text{cm}^{-1}$  band is due to the symmetric stretching of the  $\text{SiO}_4$  tetrahedra with four NBOs [27]. The very weak band at about  $335$   $\text{cm}^{-1}$  is related to the vibrations of the network modifier ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ )-NBO bonds [28,29]. At low frequencies, the asymmetric band at  $70$   $\text{cm}^{-1}$  is the so called Raman-Stokes boson peak, related to the thermal population of phonons, a feature common in Raman spectra of amorphous materials [30,31]. The band in the vicinity of  $-70$   $\text{cm}^{-1}$  is the Raman-anti-Stokes boson peak.

The Raman spectrum (b), in Fig. 2, is of the  $\text{Cr}_2\text{O}_3$  doped glass. In addition to the bands observed in the undoped glass, an intense and narrow band appears at about  $850$   $\text{cm}^{-1}$ , and a shoulder is located at about  $890$   $\text{cm}^{-1}$ . A low intensity band appears at  $365$   $\text{cm}^{-1}$  with a shoulder at its high frequency side.

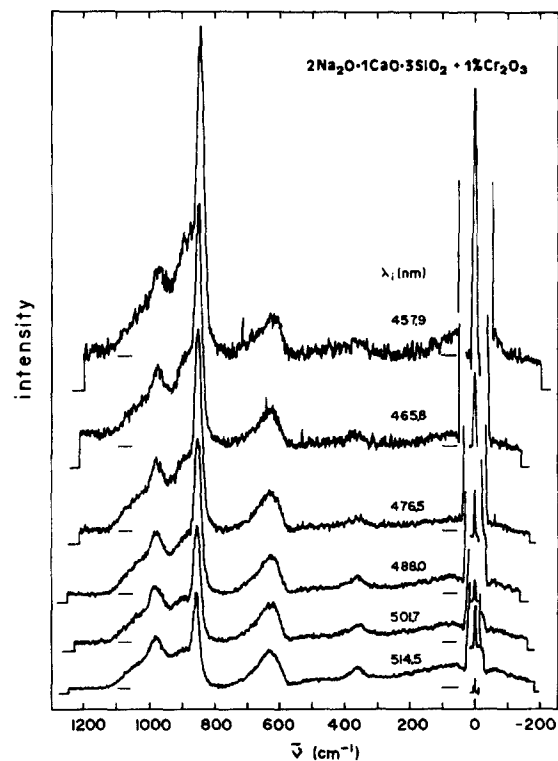


Fig. 4. Raman spectra ( $90^\circ$  scattering geometry) of the 1.0 wt%  $\text{Cr}_2\text{O}_3$  doped glass excited by the visible Ar laser lines. The spectra are normalized with respect to the intensity of the band at  $625$   $\text{cm}^{-1}$ .

A better visualization of these bands is shown in Fig. 3, which is the result of the subtraction of both spectra in Fig. 2, normalized with respect to the band at  $625\text{ cm}^{-1}$ , taken as an internal standard. The 'spectrum' which results from this subtraction is essentially similar to the spectrum of  $\text{CrO}_4^{2-}$  in aqueous solution [17].

The Raman spectra obtained with the  $90^\circ$  scattering geometry using the main visible Ar laser lines are presented in Fig. 4. The intensity of all the spectra are normalized with respect to the  $625\text{ cm}^{-1}$  band of the glass network spectrum. The intensity of the  $850\text{ cm}^{-1}$  band increases considerably when the exciting wavelength decreases, which is due to the pre-resonant Raman effect.

It must be emphasized that, with the classical  $90^\circ$  scattering geometry, there is an optical absorption of the scattered light inside the sample. The effect of the absorption in our analysis is partially removed by the normalization of the spectra with respect to the  $625\text{ cm}^{-1}$  band which is expected to be subject to similar absorption effects. In order to clarify this point, we performed micro-Raman measurements on

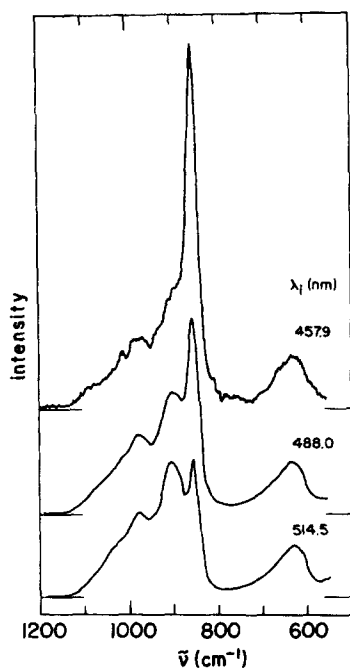


Fig. 5. Micro-Raman spectra of the same sample as that of Fig. 4, also normalized with respect to the  $625\text{ cm}^{-1}$  band.

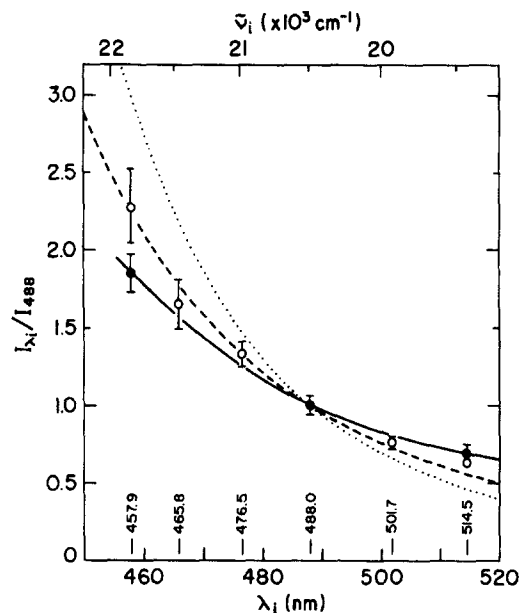


Fig. 6. Relative intensity of the  $\bar{\nu}_s = 850\text{ cm}^{-1}$  Raman bands as a function of the exciting wavelength,  $\lambda_i$ . The open circles (O) are the experimental values taken from the spectra of Fig. 4, while the close circles (●) were taken from Fig. 5. The dashed and dotted curves represent the adimensional factors  $F_B^2$  (Eq. (2)) and  $F_A^2$  (Eq. (1)), respectively, using  $\bar{\nu}_e = 27000\text{ cm}^{-1}$ ,  $\bar{\nu}_f = 40000\text{ cm}^{-1}$  and  $\bar{\nu}_i = \lambda_i^{-1}$ . The solid curve is a fit to a visual guide of the micro-Raman results. Normalization has been made so that the intensity is equal to unity for  $\lambda_i = 488.0\text{ nm}$ .

the surface of the sample, and the results are presented in Fig. 5.

Fig. 6 shows the dependence of the intensities of the  $850\text{ cm}^{-1}$  bands with the exciting wavelength taking  $I_{\lambda_i}/I_{488} = 1$  for  $\lambda_i = 488.0\text{ nm}$ . The dashed curve is the representation of Eq. (2), using the absorption frequencies of the chromate ion:  $\bar{\nu}_e = 27000\text{ cm}^{-1}$  ( $\lambda_e = 370\text{ nm}$ ) and  $\bar{\nu}_f = 40000\text{ cm}^{-1}$  ( $\lambda_f = 250\text{ nm}$ ), while the dotted line represents Eq. (1). The  $90^\circ$  scattering geometry data are better fitted by the adimensional factor  $F_B^2$  given by Eq. (2). In the case of the data obtained by a micro-Raman surface analysis, results of which are adjusted by the solid curve, the fit by Eq. (2) is less good. These results are discussed in the next section.

#### 4. Discussion

The optical absorption bands at 370 and at 250 nm of the chromate ion (Fig. 1) are due to charge

transfer between the ligand ( $O^-$ ) and the metal ion ( $Cr^{6+}$ ) [23], which produces a polarizability change of the molecular ion. While approaching the 370 nm band from higher wavelengths, there is an increase of the chromate ion polarizability. This increase produces the enhancement of the  $850\text{ cm}^{-1}$  Raman band intensity, and the pre-resonant Raman effect takes place.

The structure of silicate glasses, like other amorphous materials, is disordered for mid- and long-range. The interatomic bond lengths and bond angles have broad distributions, which is not the case for crystalline structures. These structural features are responsible for the broadening of the Raman bands of glasses by comparison with the narrower bands observed in crystalline materials with the same composition as the precursor glass [32,33].

The chromate ion Raman band at  $850\text{ cm}^{-1}$ , seen in Figs. 2–5, is narrower than the bands of the glass matrix. Spectra similar to that shown in Fig. 3 were presented by Michel and Machiroux [17] and by Braver and White [20] for chromate ions in aqueous solutions, and the band assignments are in accordance with the work of Stammreich et al. [15]. Such features lead us to conclude that the vibrational mode frequencies of the chromate ion are not influenced by the surrounding glass network. The absence of a vibrational coupling between the glass network and the chromate ions is an indication that these ions are isolated in the glass, and consequently there are no bonds such as  $\equiv Cr-O-Si \equiv$  and  $\equiv Cr-O-Cr \equiv$ . This observation agrees with that made by Braver and White [20].

Brown et al. [34] measured Raman and infrared spectra of solid  $Cr_2O_3$  and assigned the chromium–oxygen stretching and bending modes on the basis of octahedrally coordinated  $Cr^{3+}$  ions. In their Raman spectrum, the band at  $348\text{ cm}^{-1}$  is attributed to the O–Cr–O bond deformation mode  $\nu_5(F_{2g})$ . This frequency is almost the same as for the  $CrO_4^{2-}$  symmetric bending mode,  $\nu_2(E)$ , indicated in Fig. 3. No other correspondence between the  $Cr_2O_3$  Raman bands identified by Brown et al. and the  $CrO_4^{2-}$  spectrum in Fig. 3 has been found. This may be explained by the lower concentration of  $Cr^{3+}$  than  $Cr^{6+}$  ions in the glass, and also by the low polarizability changes of the  $Cr^{3+}-O$  bond during vibrations.

Fig. 6 shows that Eq. (2) gives the best fit of the experimental data obtained with the  $90^\circ$  scattering geometry. However, the fit is less good for the micro-Raman data, obtained at the sample surface, in which case the absorption of the scattered light is negligible. It is important to emphasize that the theoretical models represented by Eqs. (1) and (2) do not take into account the damping associated to the optical absorption processes. Ovander [35] showed that the theoretical models which explain the resonant Raman scattering must be modified when the damping is large. In this case, the divergence of the scattering intensity is removed for  $\bar{\nu}_i = \bar{\nu}_c$  (or  $\bar{\nu}_i = \bar{\nu}_r$ ). Loudon [36] observed that, in the case of resonance Raman scattering, the Raman tensor is always finite due to the arrangement of the electronic energy levels in bands.

This feature can be qualitatively described by the addition of a damping term in the denominator of the scattering intensity expression,  $I_s$  [1,5,36,37]. The addition of a constant term in the denominator of Eqs. (1) and (2) would change the  $I_\lambda/I_{488}$  curve, shown in Fig. 6, in such a way that the new curve would pass below the displayed curve for  $\lambda_i < 488\text{ nm}$  and above this curve for  $\lambda_i > 488\text{ nm}$ . This result is in accordance with our micro-Raman experimental data.

## 5. Conclusions

The pre-resonant Raman effect observed for chromate ion in the  $2Na_2O \cdot 1CaO \cdot 3SiO_2$  glass is qualitatively explained by the theory developed for two electronic transitions involved in the inelastic light scattering process; the dependence of the  $850\text{ cm}^{-1}$  band intensity with the exciting wavelength is better adjusted by the adimensional factor  $F_B^2$ , given by Eq. (2). The theory must be improved by the introduction of a damping term in the equations considered in order to give a better adjustment of the experimental data.

Comparison made between Raman spectra of chromate ions in liquid solutions, in crystals and in glasses show no substantial differences with respect to frequencies, width and polarization of their bands. These observations reinforce early conclusions that there is no vibrational coupling between these ions

and their vicinity, since the ions are dissolved in the glass network, coordinated by the modifier ions  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , to keep the electrical neutrality of the glass.

### Acknowledgements

One of the authors (E.C.Z.) gratefully acknowledges financial support by FAPESP (São Paulo, Brazil) (Grant Nos. 85/2619-6, 86/1677-5 and 88/2931-8). This research was also sponsored by FINEP and CNPq (Brazil).

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