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**Comment on “Theoretical analysis of the oxocarbons: structure and spectroscopic properties of croconate ion and its coordination compound with lithium” by G. M. A. Junqueira, W. R. Rocha, W. B. De Almeida and H. F. Dos Santos, *Phys. Chem. Chem. Phys.*, 2001, 3, 3499**

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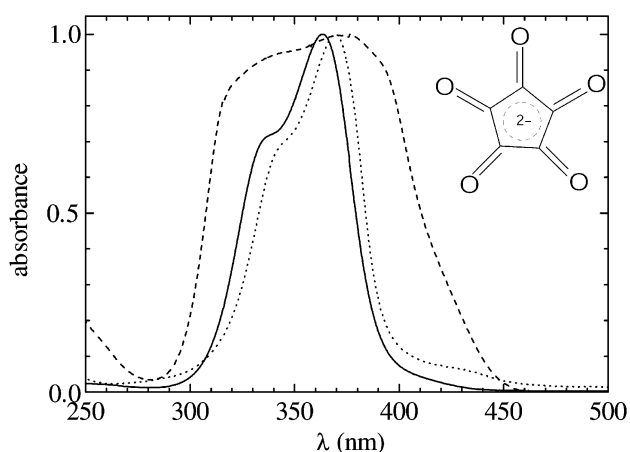
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The croconate anion,  $C_5O_5^{2-}$  (see the inset in Fig. 1) is one member of the oxocarbon series, which are planar cyclic dianions with general formula  $C_nO_n^{2-}$  ( $n = 3, 4, 5, 6$ ). As far as their Raman spectra are concerned, oxocarbon ions stand out for the unusually high intensity of several non-totally symmetric modes, which were assigned to the Jahn–Teller effect in the first allowed degenerate electronic state.<sup>1</sup> The electronic spectra of oxocarbons exhibit the typical two-peaks pattern due to the Jahn–Teller distortion of the excited electronic state. In fact, several papers on their resonance Raman and optical spectra, electronic structure and transition metal complexes have been published in which the Jahn–Teller effect plays a key role in their interpretation.<sup>2</sup> However, in a recent paper in this journal,<sup>3</sup> by using a combined theoretical approach including quantum chemistry calculations and Monte Carlo simulations, it has been proposed that the two absorption bands observed in the electronic spectrum of the croconate ion are the result of degeneracy lifted by distortions due to intermolecular interactions that occur in solution. From the Monte Carlo simulations, several clusters of one  $C_5O_5^{2-}$  anion plus two lithium cations and some water molecules are picked up and used as input in semi-empirical quantum chemistry calculations of the electronic spectra. The authors<sup>3</sup> conclude that the strong interaction between the croconate and the counterion, plus a first solvation shell, must be taken into account in

order to reproduce the positions of the two bands in the experimental electronic spectrum.

As mentioned above, the resonance Raman spectra of oxocarbon ions have been interpreted in light of the Jahn–Teller effect, so that strong implications arise from the new proposal of ref. 3, where the electronic spectra have been interpreted instead as a condensed phase effect. On the other hand, we believe that the proposition of ref. 3 can be easily verified by recording the electronic spectrum of the croconate ion in other environments. If the splitting of the electronic spectrum of the croconate ion is due to the strong interactions with the lithium cations in such a cluster as devised in ref. 3, the pattern of the electronic spectrum should be very different in other croconate salts. A stringent test would be given by a derivative synthesised recently:<sup>4</sup> tetra(n-butyl)ammonium croconate, TBCR,  $[(n-C_4H_9)_4N]_2C_5O_5 \cdot 4H_2O$ . TBCR is a very viscous ionic liquid with a low glass transition temperature ( $T_g \approx 20^\circ C$ ), and it has been used as a prototype for room temperature molten salts in a recent Raman spectroscopy study.<sup>4</sup> If the splitting in the electronic spectrum is not inherent to the  $C_5O_5^{2-}$  species (the Jahn–Teller effect) but instead due to its interaction with the cations, distinct spectra should be obtained by using a dilute solution, in which the clusters devised in ref. 3 are not favoured, or by replacing lithium by say potassium and, as a limiting case, tetra(n-butyl)ammonium. That is not the case, as one can see in Fig. 1 where absorption spectra of the croconate ion are shown in different environments. The electronic spectra of a  $0.5 \times 10^{-4}$  M aqueous solution of  $Li_2C_5O_5$  (the full line in Fig. 1) is identical to an aqueous solution of other croconate salt, including the TBCR derivative (not shown in Fig. 1). Therefore, the observed shape of the spectrum is not due to the interaction with  $Li^+$ . The splitting of the absorption band is also observed in pure TBCR with no solvent at all (the dashed line in Fig. 1), where as expected an heterogeneous broadening of the spectrum occur due to the high viscosity of the melt. The spectrum of a  $1.6 \times 10^{-5}$  M acetonitrile solution of TBCR (dotted line) is the same as in the aqueous solution, except by a blue shift of the whole (Jahn–Teller split) spectrum. Such significant solvatochromic shift indicates that interesting solvent effects on the electronic spectrum of the croconate ion do exist, which however deserve a further theoretical quantum chemistry investigation.

Therefore, the splitting of the electronic spectrum should be assigned to the croconate species itself, *i.e.* the Jahn–Teller effect, and not to a cluster between the croconate, two lithium ions and water molecules. The strong interactions devised in ref. 3 should imply major impacts on the vibrational spectra as well, for instance, splitting of the degenerate normal modes.



**Fig. 1** Electronic spectra of the croconate ion: a  $0.5 \times 10^{-4}$  M aqueous solution of  $Li_2C_5O_5$  (full line), pure  $[(n-C_4H_9)_4N]_2C_5O_5 \cdot 4H_2O$  (TBCR) at room temperature (dashed line), and a  $1.6 \times 10^{-5}$  M acetonitrile solution of TBCR (dotted line).

This is also contrary to experimental findings, as the Raman spectra of the croconate ion is very much the same irrespective of the counterion, including the TBCR case. It is worth mentioning that the authors in ref. 3 have found good agreement between the theoretical vibrational spectra calculated for the *free* anion and the experimental one recorded in solid phase or solution. In fact, the dynamics of the oxocarbon ions  $\text{C}_4\text{O}_4^{2-}$  and  $\text{C}_5\text{O}_5^{2-}$  in aqueous solution have been investigated previously by a detailed Raman bandshape analysis,<sup>2</sup> which does not corroborate the picture given in ref. 3. In summary, we showed in this Comment that the proposal of ref. 3, namely that the structure observed in the electronic spectrum of the croconate ion is not due to the Jahn–Teller distortion but instead to intermolecular interactions in solution, is not corroborated by the experimental data. The clusters devised in that reference should be disfavoured by working with a dilute solution or simply by replacing lithium by other cations, whereas the experimental spectra in a given solvent are in fact the same whatever the counterion. The same pattern in the electronic spectrum has been found in a limiting case, namely

tetra(n-butyl)ammonium croconate, which is a further indication that such clusters are not the reason for the two bands.

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