

Raman spectroscopy and molecular mechanics in the investigation of molecular structure: calcium, strontium, barium and copper(II) monochloroacetates

J.J.C.Teixeira-Dias and R. Fausto

The University Chemical Department, 3049 Coimbra, Portugal

Abstract - Molecular mechanics is used to provide information on the stable conformations of the monochloroacetic acid molecule. In the most stable form, the C-Cl is in the COO plane (*syn*), while in the other form (*gauche*) the Cl-C-C=O dihedral angle is in the 131° region. Thus in the *syn* form, the bond dipoles associated with the C-Cl and C=O bonds are approximately aligned, leading to a C=O bond stronger than in the less stable conformer and, by consequence, to a larger C=O stretching frequency for this form.

The Raman spectra of Ca, Sr, Ba and Cu(II) monochloroacetates in crystalline phases have been recorded and interpreted to assess the relative importance of the mutual interactions of the metal-metal and metal-ligand bonds and the nature of the metal-metal bond in these systems. The preferred conformations around the C_α-C single bond of the coordinating monochloroacetic acid molecules have also been studied and correlated with our previous theoretical and experimental results on the pure acid.

INTRODUCTION

Raman spectra has been increasingly used in the structural elucidation of molecular systems, coordination compounds included. In general, information on isolated molecular systems is required, as the interpretation of spectra often relies on spectral comparisons and intermolecular effects may be relevant. As isolated systems are not always amenable to experiment, theoretical models should be relied upon.

In this work, Raman spectra of calcium, strontium, barium and copper (II) monochloroacetates are presented and discussed. Molecular mechanics is used to provide information on the monochloroacetic acid molecule.

COMPUTATIONAL AND EXPERIMENTAL METHODS

The calculations were carried out with the fast convergent energy minimization CFF program of Niketic and Rasmussen (ref.1), adapted to a DG/Eclipse MV8000 computer. Detailed information on computational algorithms and the original program can be found in refs. 1 and 2.

Raman spectra were recorded on a Ramalog double spectrometer, 0.85 m, $f/7.8$, Spex model 1403, equipped with holographic gratings with 1800 grooves/mm. A detector assembly containing a Hamamatsu type R928 photomultiplier tube, for 190 to 860 nm, multi alkali, in thermoelectric cooled housing, was used. The light source was a Spectra-Physics Ar^+ laser (model 164-05), whose output at 476.5 nm was adjusted to provide 20-40 mW at the sample position.

The chemicals were prepared as described in ref. 3 and purified by standard methods, prior to spectra recording.

RESULTS AND DISCUSSION

Monochloroacetic acid molecule

Rotational isomerism in this molecule has been the subject of various studies (refs. 4 to 12) though a large majority of them refer to condensed phases. Results for the isolated molecule or the gas phase come from infrared (refs. 9 and 11), electron diffraction (ref. 10) and *ab initio* MO calculations (refs. 10 and 12). In particular, electron diffraction suggests the occurrence of three distinct conformers (Fig. 1) resulting from rotation around the $\text{C}_\alpha\text{-C}$ bond. The more stable conformer corresponds to the Cl-C-C=O dihedral angle equal to 0° (*syn* form). *Ab initio* calculations (STO-3G) confirm that this is the lowest energy conformation (ref. 12).

Figure 2 shows the potential energy curve for the rotation around the $\text{C}_\alpha\text{-C}$ bond as calculated by molecular mechanics using the PF1 force field (refs. 13 and 14). These results indicate the occurrence of only two distinct conformers (*syn* and *gauche*), the *syn* form being the more stable. As it is shown in Table 1, the structural parameters calculated by molecular mechanics are in excellent agreement with the corresponding electron

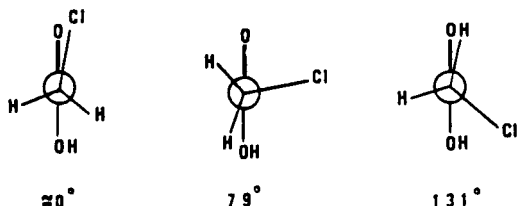


Fig. 1. Conformers of monochloroacetic acid according to ref. 10.

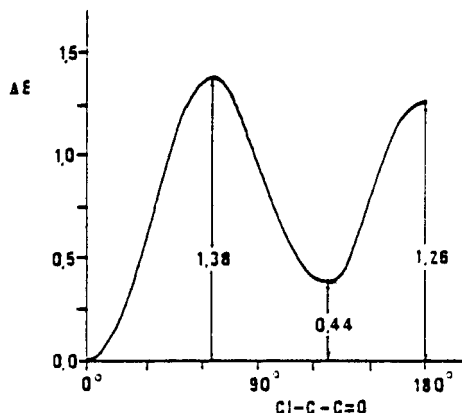


Fig. 2. Potential energy curve for rotation around the $\text{C}_\alpha\text{-C}$ bond in the monochloroacetic acid molecule as calculated by molecular mechanics using the PF1 force field (ref. 13).

Table 1. Experimental and calculated structures for monochloroacetic acid

Parameter	Experimental (ref. 10)	Calculated
C-C	150.9	150.5
C-Cl	177.9	178.1
C-H	109.9	109.6
C-O	135.4	133.6
C=O	122.4	120.0
O-H	98.3	97.0
C-C-Cl	112.8	112.3
C-C-H	109.5	109.8
C-C-O	110.7	108.4
C-C=O	126.2	125.8
Cl-C-H	107.7	107.9
H-C-H	109.5	109.1
C-O-H	106.0	106.9
O=C-C-Cl (<i>syn</i>)	0.0	0.0
O=C-C-Cl (<i>gauche</i>)	131.0	131.6

Bond lengths in pm; angles in degrees.

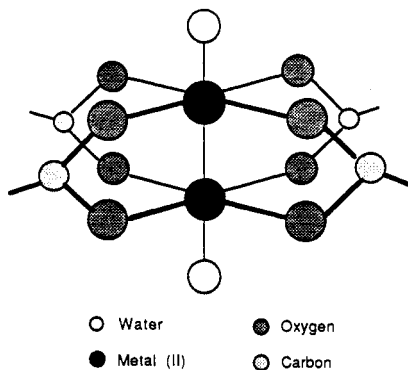


Fig.3. Molecular structure of metal (II) monochloroacetates (schematic).

diffraction results. In particular, the calculated Cl-C-C=O dihedral angles for the *syn* and *gauche* forms agree very well with the electron diffraction values.

As it was mentioned, the third conformer suggested by electron diffraction is not confirmed by molecular mechanics. In addition, experimental results for other α -chloro substituted carbonylic compounds show that a Cl-C-C=O dihedral angle of approximately 60° corresponds to an energy maximum, not a minimum (ref. 15). Thus, the consideration of that particular conformation as an energy minimum should probably result from approximations used in the interpretation of the electron diffraction results, like the rigid rotor approximation and the non-optimization of a number of structural parameters.

Molecular mechanics shows also that the CCl angle increases by approximately 2° in the *gauche* \rightarrow *gauche* transition conformation, as the chlorine atom eclipsing the OH group is repelled by the lone pairs of electrons on the hydroxylic oxygen atom.

Ca, Sr, Ba and Cu monochloroacetates

The structure of a few carboxylate complexes of divalent metal ions (Fig.3) has been determined by X-ray crystallography and subsequently confirmed by analysis of infrared spectra (refs. 16 to 20). While X-ray crystallography data has not been obtained for the compounds herein

studied, analysis of Raman spectra indicates a similar structure for Ca, Sr, Ba and Cu(II) monochloroacetates. In particular, the symmetric and antisymmetric stretching frequencies of COO^- vary in the same direction along the Ca^{2+} , Sr^{2+} , Ba^{2+} series (Table 2), suggesting approximately equivalent CO bonds in the carboxylate ligands.

One interesting feature of the Raman spectra of these complexes is the occurrence of pairs of bands, each pair associated with the same type of vibration. As most of these correspond to frequency separations larger than 20 cm^{-1} , they cannot be ascribed to crystal splitting effects. On the other hand, while localized hydrogen bonding cannot be excluded as a possible cause, the most plausible origin of those pairs of bands comes from the different orientations of the CHCl_2 group in the carboxylate ligands. In addition, comparison of the carbonylic stretching frequency region in the pure monochloroacetic acid with the region of the antisymmetric stretching mode in the studied complexes (Fig.4) supports that conclusion and further indicates that the *syn* form - the more polar form corresponding to the higher vibrational carbonylic frequency (refs. 14 and 15) - is more populated in the calcium compound.

Table 2. Raman COO^- stretching frequencies (cm^{-1}) of Ca^{2+} , Sr^{2+} and Ba^{2+} monochloroacetates.

	Ca	Sr	Ba
$\nu(\text{COO}^-)_{\text{as}}$	1619	1617	1609
	1602	1580	1581
$\nu(\text{COO}^-)_{\text{s}}$	1454	1446	1433
	1407	1405	1402

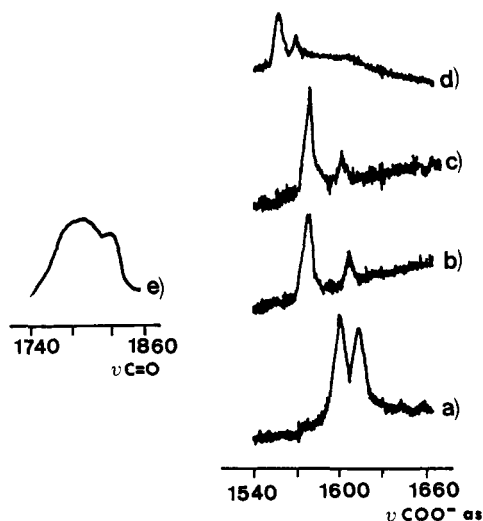


Fig. 4. Raman bands of COO^- antisymmetric stretching modes of a) Ca^{2+} , b) Sr^{2+} , c) Ba^{2+} , d) Cu^{2+} monochloroacetates and e) infrared bands of $\text{C}=\text{O}$ stretching modes of pure monochloroacetic acid (ref. 12).

Comparison of the relative intensities of the pairs of Raman bands along the series Ca^{2+} , Sr^{2+} , Ba^{2+} leads to ascribe bands to conformers. In all the cases, the *syn/gauche* relative intensities for the Ca^{2+} complex are very different from the Sr^{2+} and Ba^{2+} compounds while these originate similar values.

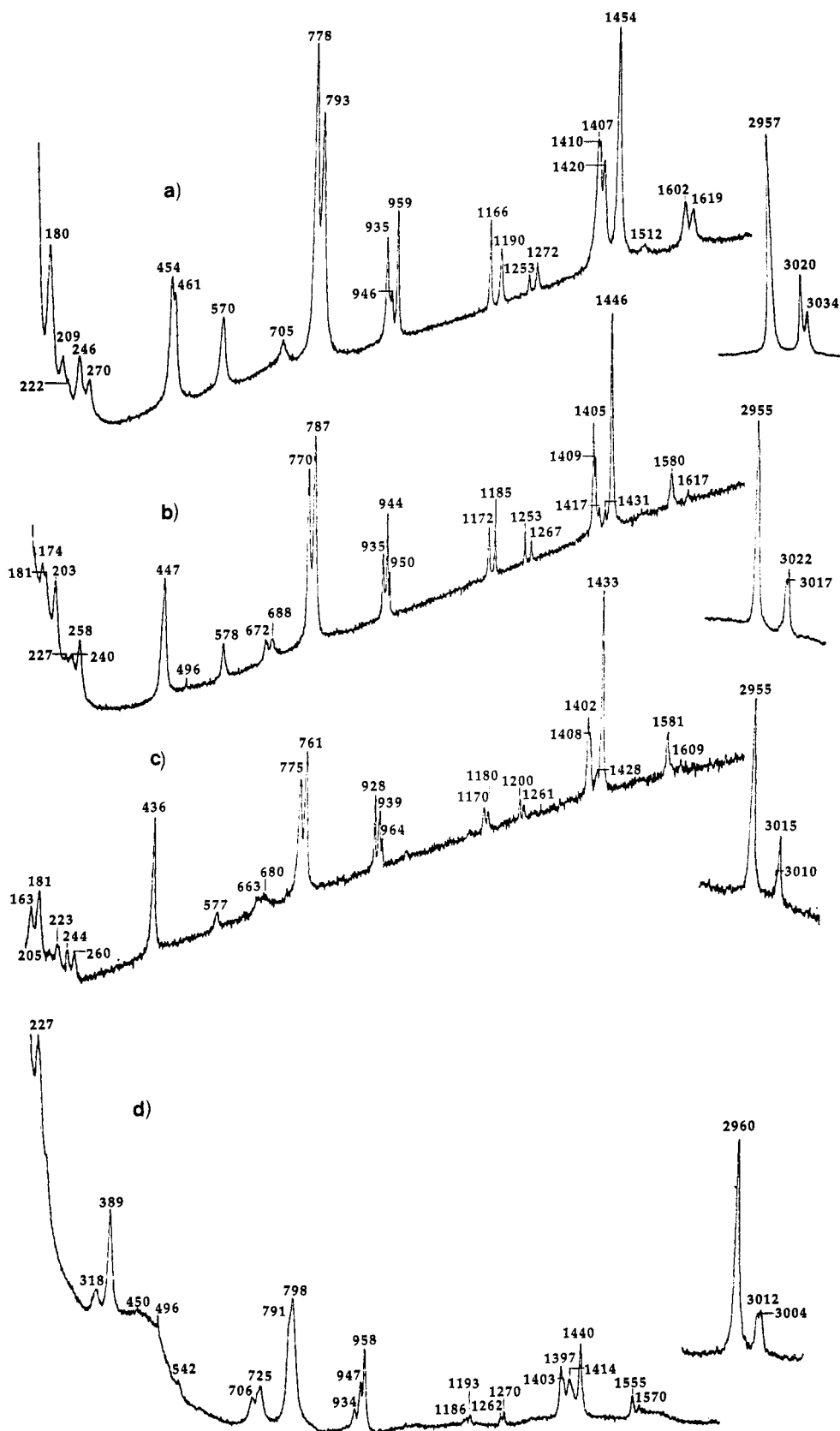


Fig. 5. Raman spectra of crystalline monochloroacetates. a) Ca²⁺, b) Sr²⁺, c) Ba²⁺ and d) Cu²⁺

In order to understand the varying degrees of M-M and M-L interactions in the studied complexes, Raman frequencies are plotted against the ionic radius (Fig.6) and the first ionization potential of the metal atoms (Fig.7).

While clear trends are observed in both cases for the Ca^{2+} , Sr^{2+} , Ba^{2+} series, the ionic radius provides a stronger correlation of vibrational frequencies. In addition, the Raman frequencies for the Cu^{2+} complex do not fall in the same straight lines as the remaining complexes, suggesting that a different type of M-L interaction, probably involving the d-orbitals of the transition metal ion, might take place in this case. In fact, the p delocalization over the five membered ring formed by each carboxylate group and the two metal ions should involve the d-orbitals of the transition metal ions and is expected to lead to a decrease of

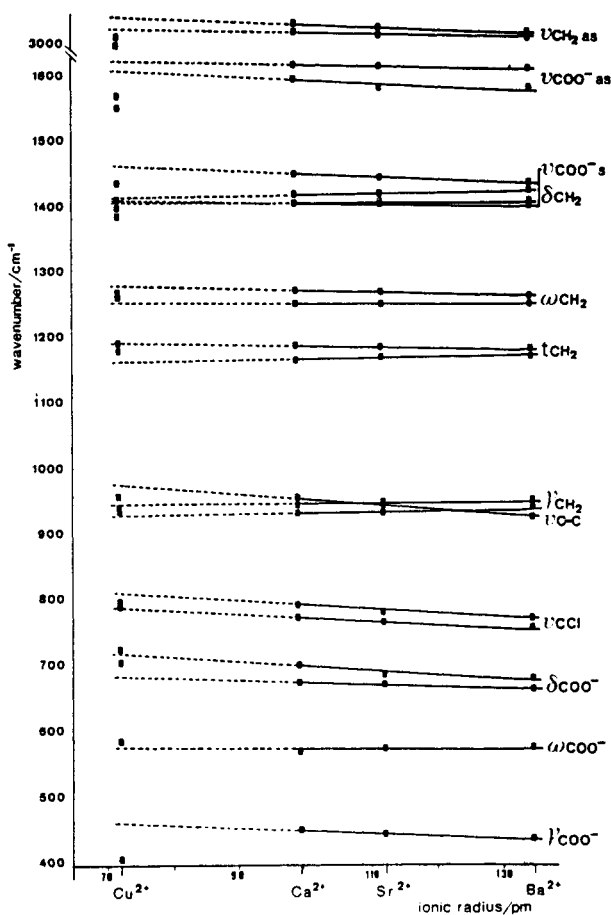


Fig. 6

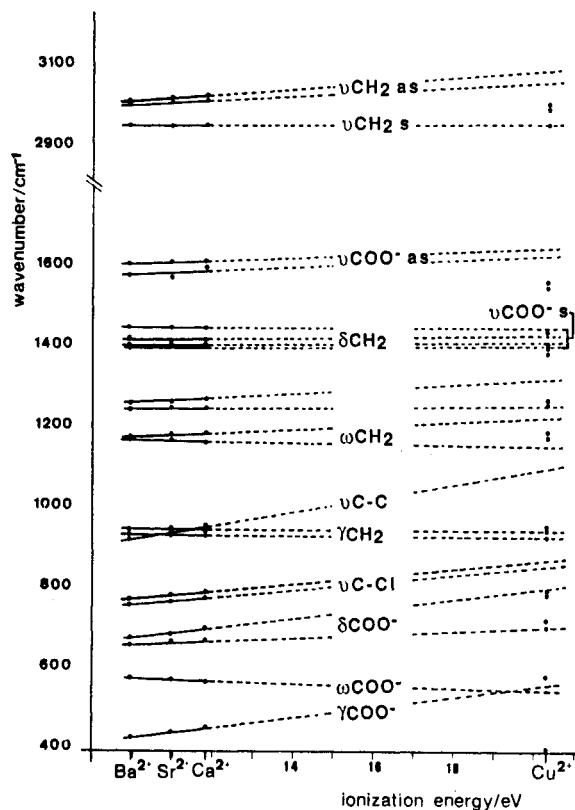


Fig. 7

Fig. 6 and 7. Raman frequencies of Ca^{2+} , Sr^{2+} , Ba^{2+} and Cu^{2+} monochloroacetates vs. ionic radius of metal ion and vs. first ionization energy of metal atom.

Table 3. Raman COO⁻ bending frequencies (cm⁻¹) of Ca²⁺, Sr²⁺, Ba²⁺ and Cu²⁺ monochloroacetates.

Ca	Sr	Ba	Cu
705	688	680	725
677	672	663	706

electronic density on the carboxylate group, as part of this density moves to the metal ions. Thus, the COO⁻ stretching frequencies should decrease as it is, in fact, observed in the Raman spectra, in particular, for the antisymmetric mode which reduces by approximately 35 cm⁻¹.

In addition, a stronger M-M interaction is expected to lead to an increase in the M-O and C-O bond distances (ref. 21). In particular, the increase in the C-O bond length leads to a decrease in the stretching frequencies of the carboxylate group. On the whole, the M-M interaction follows the order Cu >> Ba > Sr > Ca.

In those compounds where the carboxylate acts as a quelate surrounding two directly bonded metal atoms, X-ray crystallographic results show that the O-C-O angle is very sensitive to the M-M distance and increases with it. In turn, an increase in the O-C-O angle implies a force constant reduction, thus leading to a frequency decrease in the corresponding vibrational mode (Table 3). The sensitivity of this vibrational frequency to the M-M distance can certainly be used as a way of determining both the M-M bond length and its bond strength from the vibrational frequency. While the largest sensitivity to the variation in the M-M length is expected from the M-O-C deformation frequency due to the small value of its force constant, the corresponding band has low frequency and so is of difficult access and interpretation.

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REFERENCES

1. S.R.Niketic and Kj.Rasmussen, The Consistent Force Field: A Documentation, Lecture Notes in Chemistry, Vol.3, Springer-Verlag, Heilderberg (1977).
2. Kj. Rasmussen, Potential Energy Functions in Conformational Analysis, Lecture Notes in Chemistry, Vol.37, Springer-Verlag, Heilderberg (1985).

3. W.G.Bateman and A.B.Hoel, J.Am.Chem.Soc., **36**, 2517 (1914).
4. H.Negita, J.Chem.Phys., **23**, 214 (1955).
5. J.R.Barcelo, M.P.George and C.Otero, J.Chem.Phys., **28**, 1230 (1958).
6. V.H.Johansen, Z.Phys.Chem., **227**, 305 (1964).
7. R.J.Jakobsen and J.E.Katon, Spectrochim.Acta, **A29**, 1953 (1973).
8. D.Sinha, J.E.Katon and R.J.Jakobsen, J.Mol.Struct., **20**, 381 (1974).
9. L.I.Kozhevina, V.M.Bilobrov, V.A.Panichikina and E.V.Titov, Zh.Strukt.Khim., **20**, 405 (1979).
10. J.L.Derissen and J.M.J.M.Bijen, J.Mol.Struct., **29**, 153 (1975).
11. J.M.J.M.Bijen, Ph.D.thesis, Conformation and Internal Hydrogen Bonding. Investigation of Derivatives of Formic and Acetic acids in Vapour, Rijksuniversiteit Utrecht, Utrecht (1974).
12. V.M.Bilobrov, V.A.Panichkina and E.V.Titov, Zh.Strukt.Khim., **22**, 69 (1981).
13. J.J.C.Teixeira-Dias and R.Fausto, J.Mol.Struct., **144**, 199 (1986).
14. R.Fausto and J.J.C.Teixeira-Dias, J.Mol.Struct., **144**, 225 (1986).
15. R.Fausto, Ph.D.thesis, Conformational Analysis of Oxygen and Sulphur Containing Compounds, University of Coimbra, Coimbra (1987).
16. M.Melnik, Coord.Chem.Rev., **42**, 259 (1982), and references therein mentioned.
17. K.Smolander, Inorg.Chim.Acta, **114**, 1 (1986).
18. V.M.Rao, D.N.Sathyanarayana and H.Manohar, J.Chem.Soc.Dalton Trans., 2167 (1983).
19. P. de Meiter, S.R.Fletcher and A.C.Skapski, J.Chem.Soc.Dalton Trans., 2575 (1973).
20. A.V.R.Wanier and P.S.Narayanan, Spectrochim.Acta, **23A**, 1061 (1967).
21. Y.B.Koh and G.G.Christoph, Inorg.Chem., **18**, 1122 (1979).