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Solid-state linear polarized IR-spectroscopy of croconic and rhodizonic acids

Research Article

Tsonko Kolev[1,2*], Bojidarka B. Koleva[3*], Michael Spiteller[4]

[1] *Institute of Organic Chemistry, BAS, Acad. G. Bonchev Str. build. 9, 1113 Sofia, Bulgaria*

[2] *Plovdiv University, Faculty of Chemistry, 25, Tzar.Assen, Str., 4000 Plovdiv, Bulgaria*

[3] *Sofia University, Faculty of Chemistry, 1, J. Bourchier, Blvd. 1164 Sofia, Bulgaria*

[4] *Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany*

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Abstract: The applications of linear-polarized IR-spectroscopy to oriented colloid suspensions in a nematic host are demonstrated with croconic and rhodizonic acids. The experimental IR vibrational assignments of the solid-state of both neutral compounds are presented. Assignments are supported by theoretical quantum chemical calculations and vibrational analysis at the DFT level of theoretical approximation with the 6-311++G** basis set.

Keywords: *Croconic acid • Rhodizonic acid • IR-LD spectroscopy • Solid-state • Vibrations*

1. Introduction

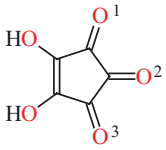
Oxocarbons, compounds with general formula $(C_nO_n)^{2-}$ and cyclic structures have been extensively studied due to their interesting fundamental chemical aspects and applications in chemical technology and analytical practice [1-10]. For example, rhodizonic acid has been used as an analytical reagent for Fe, Pb and Ba. In general the oxocarbons can be used as photoreceptors and more recently their non-linear optical properties have been investigated in order to use these compounds as organic semiconductors. The oxocarbons all have planar D_{nh} symmetry. The nonbenzenoid aromatic D_{6h} and enediolate C_{2v} valence tautomers of the relatively unstable rhodizonate dianion have been generated in situ and stabilized by hydrogen bonding with (3-hydroxyphenyl) urea and 1,1′-ethylenediurea, respectively, in two novel crystalline inclusion compounds. Detailed Raman investigations of a series of oxocarbons have been done [11-14]. However, up to now a systematic studies of the IR-spectroscopic properties of the neutral croconic and rhodizonic acids have not been carried out. For this reason we conducted an IR-spectroscopic study of both the acids depicted in Scheme 1, by means of solid-state linear-polarized (IR-LD) methods of oriented colloid suspensions in a nematic host. Quantum chemical calculations at Density Functional Theory(DFT) level of theory with the 6-311++G** basis set are performed with a view to obtaining the electronic structure and vibrational spectra of both the compounds.

2. Experimental Procedures

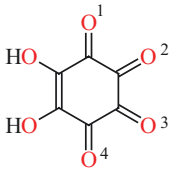
Croconic and rhodizonic acids were obtained from Merck (Germany).

IR-spectroscopic measurements over the range 4000 – 400 cm^{-1} were obtained on a Bruker 113v FT-IR spectrometer (resolution 2 cm^{-1}, 250 scans). A Specac

* *E-mail: koleva@orgchm.bas.bg*



[A]

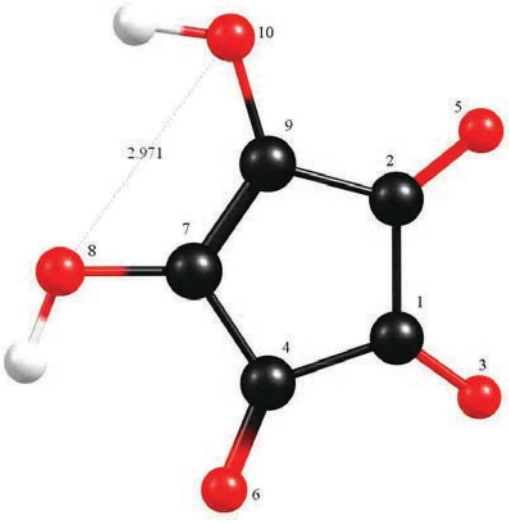


[B]

Scheme 1. Chemical diagrams of croconic [A] and rhodizonic acids [B].

wire-grid polarizer was used. Oriented solid samples were obtained as a suspension in a nematic liquid crystal of the 4'-cyano-4'-alkylbicyclohexyl type (ZLI 1695, Merck). This new orientation solid-state method [15] used in linear-dichroic infrared (IR-LD) spectroscopy for accuracy, precision and the influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands as well as the optimization of experimental conditions and an experimental design for quantitative evaluation of the impact of four input factors have been presented [16-18]. The nature and balance of the forces in the nematic liquid crystal suspension system, the mathematical model for their clearance, morphology of the suspended particles and the influence of the space system types on the degree of orientation *i.e.* ordering parameter have been shown [19] using five liquid crystals and fifteen compounds. Applicability of the latter approach for experimental IR-spectroscopic band assignment and especially for obtaining structural information has been demonstrating in a series of organic systems and metal complexes [20], Cu(II) complexes [21], polymorphs [22], codeine derivatives [23], peptides and their Au(III) complexes, hydrochlorides and hydrogensquarates [24-26].

Quantum chemical calculations were performed using the GAUSSIAN 98 program package [27] and the output files were visualized by means of the ChemCraft program [28]. Geometries of both acids (Scheme 1) were optimized at DFT level using the 6-311++G** basis set. In the second case B3LYP, which combines Becke's three-parameter non-local exchange functional with the correlation function of Lee, Yang and Parr [29,30] was used. Molecular geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm [31]. For every structure the stationary points found on the molecular potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. Absence of imaginary frequencies and negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima on the potential energy hypersurfaces. The calculation of vibrational frequencies and infrared intensities were checked to determine which level of



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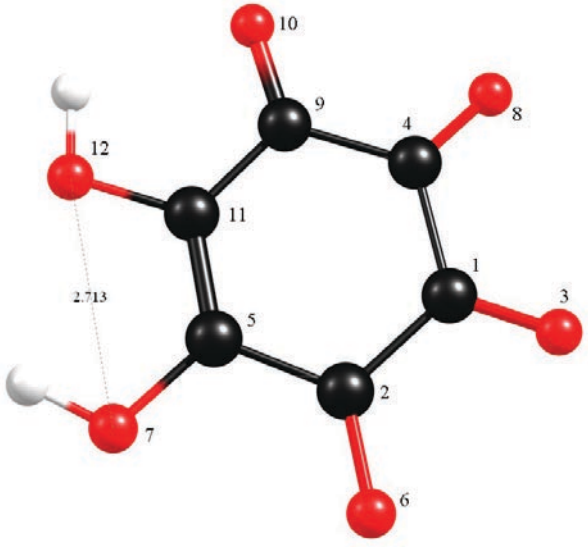


B

Scheme 2. Geometry of the most stable conformers of croconic [A] and rhodizonic acids [B].

calculations agrees best with the experimental data. B3LYP/6-311++G** data, scaled by the empirical scaling factor 0.9614 [32] gave the best correspondence between the experimental and theoretical values.

3. Result and Discussion

3.1. Theoretical calculations

Both croconic and rhodizonic acid are characterized with stable conformers, depicted in Scheme 2A and B with E_{rel} of 0.2 and 0.4 kJ/mol, respectively. The structures are stabilized by means of intramolecular

Table 1. Calculated geometry parameters, i.e. bond lengths [Å] and angles [o] of croconic and rhodizonic acids using atom numbering given in Scheme 2.

Croconic acid [A]		Rhodizonic acid [B]	
Name definition	Bond lengths [Å]	Name definition	Bond lengths [Å]
R(1,2)	1.433	R(1,2)	1.528
R(1,3)	1.259	R(1,3)	1.231
R(1,5)	1.516	R(1,4)	1.530
R(2,4)	1.369	R(2,5)	1.470
R(2,9)	1.424	R(2,6)	1.238
R(5,6)	1.244	R(4,8)	1.232
R(5,7)	1.522	R(4,9)	1.510
R(7,8)	1.247	R(5,7)	1.354
R(7,9)	1.490	R(5,11)	1.370
R(9,10)	1.277	R(9,10)	1.252
		R(9,11)	1.450
		R(11,12)	1.369
Name definition	Bond angles [°]	Name definition	Bond angles [°]
A(2,1,3)	130.0(2)	A(2,1,3)	120.2(2)
A(2,1,5)	103.9(1)	A(2,1,4)	119.6(5)
A(3,1,5)	126.0(5)	A(3,1,4)	120.1(1)
A(1,2,4)	126.6(0)	A(1,2,5)	117.0(6)
A(1,2,9)	115.0(3)	A(1,2,6)	120.5(0)
A(4,2,9)	118.3(6)	A(5,2,6)	122.4(2)
A(1,5,6)	126.2(7)	A(1,4,8)	120.9(2)
A(1,5,7)	108.2(5)	A(1,4,9)	117.8(5)
A(6,5,7)	125.4(6)	A(8,4,9)	121.2(1)
A(5,7,8)	125.9(2)	A(2,5,7)	116.1(6)
A(5,7,9)	106.0(7)	A(2,5,11)	122.3(3)
A(8,7,9)	128.0(0)	A(7,5,11)	121.4(9)
A(2,9,7)	106.7(1)	A(5,7,13)	111.2(7)
A(2,9,10)	122.9(0)	A(4,9,10)	122.9(0)
A(7,9,10)	130.3(8)	A(4,9,11)	117.9(2)
		A(10,9,11)	119.1(6)
		A(5,11,9)	125.1(6)
		A(5,11,12)	117.5(8)
		A(9,11,12)	117.2(5)
Name definition	Dihedral angles [°]	Name definition	Dihedral angles [°]
D(3,1,2,9)	179.9	D(3,1,2,5)	179.9
D(5,1,2,4)	179.9	D(4,1,2,6)	179.9
D(2,1,5,6)	179.9	D(2,1,4,8)	179.9
D(3,1,5,7)	179.9	D(3,1,4,9)	179.9
D(1,2,9,10)	179.9	D(1,2,5,7)	179.9
D(4,2,9,7)	179.9	D(6,2,5,11)	179.9
D(1,5,7,8)	179.9	D(1,4,9,10)	179.9
D(6,5,7,9)	179.9	D(8,4,9,11)	179.9
D(5,7,9,10)	179.9	D(2,5,11,12)	179.9
D(8,7,9,2)	179.9	D(7,5,11,9)	179.9
		D(4,9,11,12)	179.9
		D(10,9,11,5)	179.9

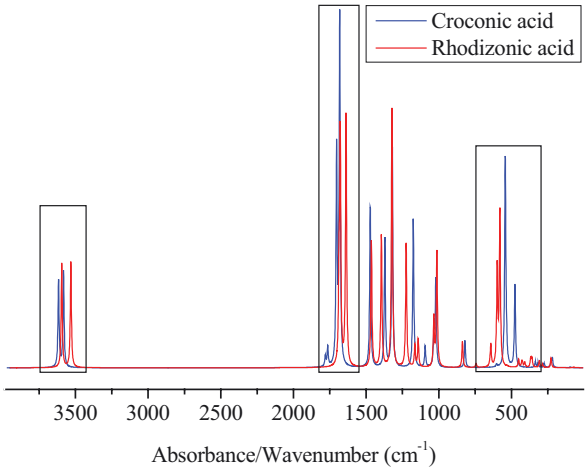
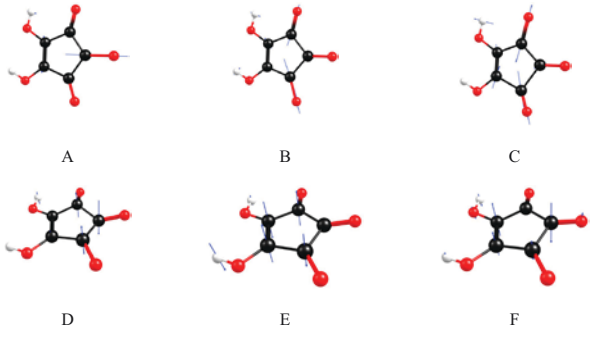


Figure 1. Theoretical IR-spectra of croconic and rhodizonic acids.



Scheme 3. Selected transition moments in croconic acid.

OH…O hydrogen bonds with lengths of 2.971 and 2.713 Å, respectively. The molecules are flat with a deviation of the total planarity less then 0.1° and 0.4°, respectively. The optimized bond lengths and angles are reported in Table 1.

The calculated IR-spectra of both the acids studied are depicted in Fig. 1. Two absorbtion bands corresponding to ν_{OH} stretching vibration are predicted at 3617 cm^{-1} and 3582 cm^{-1}. The first corresponds to the vibration of the free OH group, while the second one corresponds to intramolecular hydrogen bonded OH group. Within the 1800 – 1500 cm^{-1} IR-spectroscopic region a series of bands belonging to stretching vibrations of $\nu_{C=O}$ and $\nu_{C=C}$ are present. Using the atom numbering in Scheme 1, the band at 1781 cm^{-1} belongs to $\nu_{C=O2}$, while the 1764 cm^{-1} and 1703 cm^{-1} bands belong to $\nu^{s}_{C=O}$ and $\nu^{as}_{C=O}$ of $C=O^1$ and $C=O^3$ groups, resepctively (Scheme 3A-C). The obtained result is similar to those of the squaric acid, where the $\nu^{s}_{C=O}$ is at higher frequency than the $\nu^{as}_{C=O}$ vibration. The $\nu_{C=C}$ stretching vibrations is predicted at 1633 cm^{-1}. The out-of-plane modes of croconic acid are predicted at 800 cm^{-1}, 560 cm^{-1} and 510 cm^{-1}, respectively (Scheme 3D-F). The ν_{OH} bending vibration is predicted at 522 cm^{-1}.

Scheme 4. Selected transition moments in rhodizonic acid.

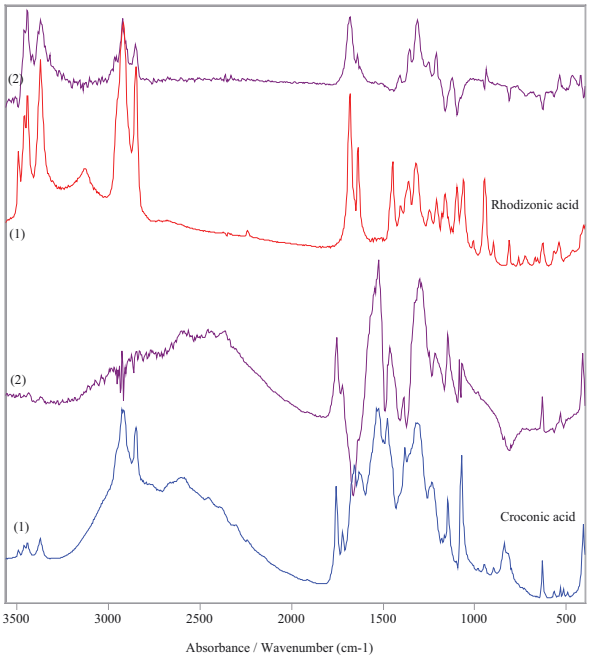


Figure 2. Non-polarized IR-(1) and difference IR-LD (2) spectra of croconic and rhodizonic acid.

The corresponding ν_{OH} stretching vibrations of free and hydrogen bonded OH groups in rhodizonic acid are obtained at 3595 cm^{-1} and 3532 cm^{-1}, resepctively. Within 1800 – 1500 cm^{-1} are obtained a series of bands at 1737 and 1710 cm^{-1} belonging to $\nu^{as}_{C=O}$ and $\nu^{s}_{C=O}$ of $C=O^2$ and $C=O^3$ groups (see Scheme 1). The second maximum is a combination of $\nu_{C=O}$ and $\nu_{C=C}$ stretching vibrations. The $\nu_{C=O}$ modes of $C=O^1$ and $C=O^4$ groups are at 1686 cm^{-1} and 1638 cm^{-1}, while the $\nu_{C=C}$ band is at 1678 cm^{-1} (Scheme 4A,B). Using the fact that in solid state the rhodizonic acid can de described as molecule with D_{6h} symmetry, the bands at 870, 743 and 451 cm^{-1} corresponds to out-of-plane modes, while those at 817 and 568 cm^{-1} – to in-plane ones. The ν_{OH} is predicted at 642 cm^{-1} (Fig. 1).

3.2. Polarized IR-LD spectroscopy

The non-polarized IR- and difference IR-LD spectra of both acids are depicted in Fig. 2. The interpretation of the IR-spectra by means of the reducing difference procedure is carried out through deconvolution and curve fitting (Fig. 3) for determination of the peak positions and corresponding integral absorbencies.

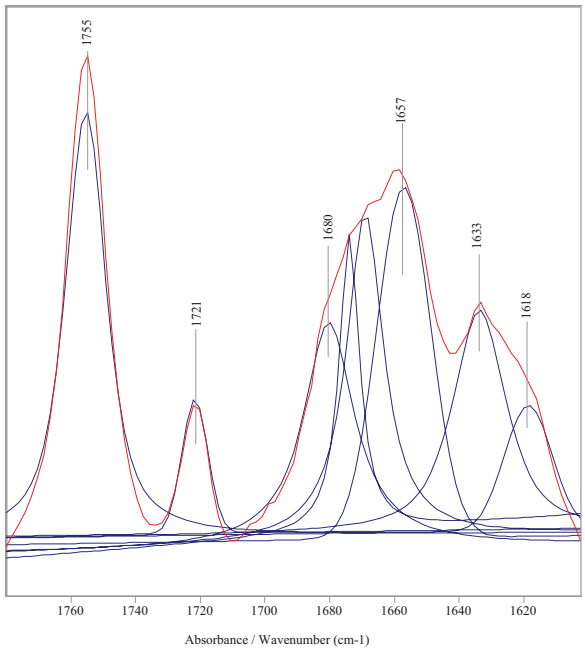


Figure 3. Curve-fitted IR-spectrum of croconic acid within the IR-region of 1780 – 1600 cm^{-1}.

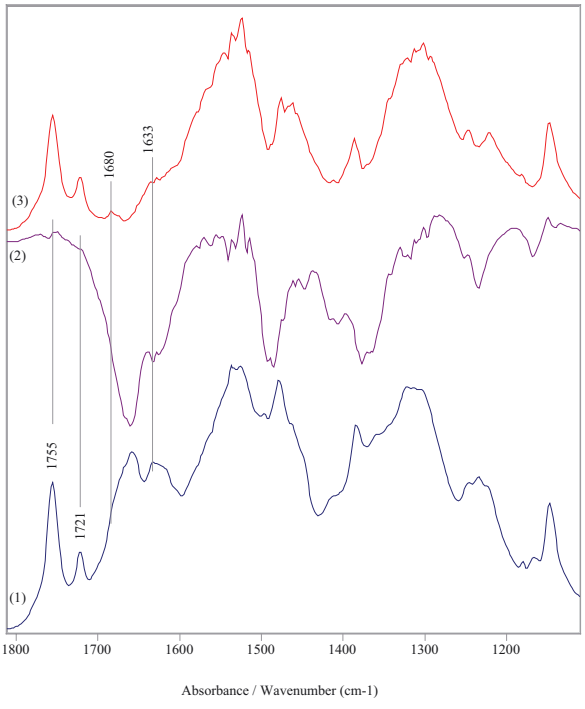


Figure 4. Non-polarized IR-(1) and reduced IR-LD spectra of croconic acid after elimination of the bands at 1755 cm^{-1} (2) and 1680 cm^{-1} (3).

In both compounds a significant degree of macro-orientation of suspended particles [16-18] is obtained, leading to an adequate interpretation of corresponding polarized IR-spectra.

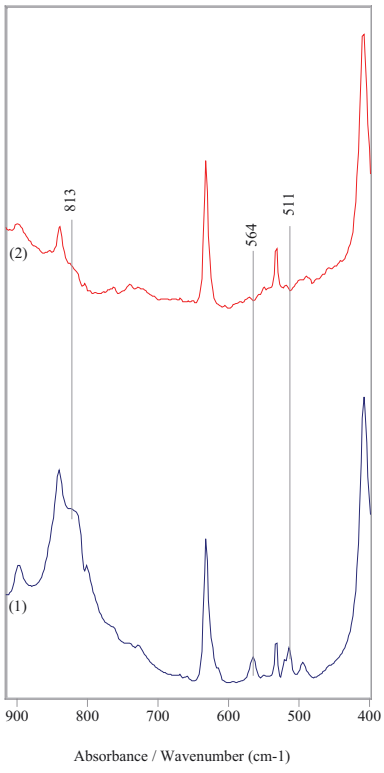


Figure 5. Non-polarized IR-(1) and reduced IR-LD spectra of croconic acid after elimination of the band at 813 cm^{-1} (2).

The IR-spectrum of croconic acid is characterized by a broad absorbtion band within 3300 – 2000 cm^{-1} (Fig. 2.1) assigned to ν_{OH} stretching vibration of the strong hydrogen bonded OH group. For the whole IR-spectroscopic pattern is observed an Evans's hole effect [32,33], like in the case of suqaric acid. The high frequency shifted bands within 1800 – 1500 cm^{-1} are the strong bands at 1755 cm^{-1} and 1721 cm^{-1} (Fig. 3). The obtained differences of 26 cm^{-1} and 43 cm^{-1} between the experimental and theoretical data can be explained primarily by the strong hydrogen bonding in solid-state with participation of C=O groups as well. A direct assignment of the origin of these bands follows by the application of reducing difference procedure for polarized IR-LD spectra interpretation (Fig. 4.2). As can be seen, both the bands are eliminated in equal dichroic portion indicating the $\nu_{C=O2}$ and $\nu^{s}_{C=O}$ origin of of C=O[1] and C=O[3] fragments, respectively (Scheme 1). This result is in accordance with theoretical data since both the transition moments are co-linear in croconic acid (Schemes 3A and B).

The elimination of the bands at 1680 cm^{-1} and 1633 cm^{-1} at equal dichroic ratio (Fig. 4.3) proves their character of $\nu^{as}_{C=O}$ and $\nu_{C=C}$ vibration, which transition moments are co-linear. The other band is at 785 cm^{-1}. The other predicted bands correlated well with the

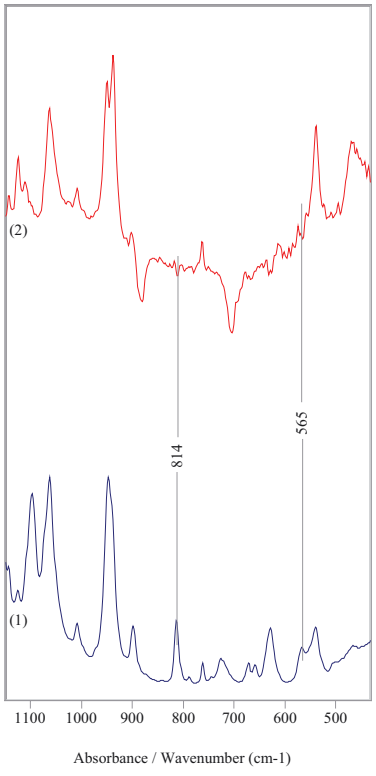


Figure 6. Non-polarized IR-(1) and reduced IR-LD spectra of rhodizonic acid after elimination of the band at 814 cm^{-1} (2).

experimental ones. Only the ν_{OH} is high frequency shifted by 291 cm^{-1}, due to participation of OH in hydrogen bonding. Direct evidence of the assignment follows from the elimination of this band with a maxima at 564 cm^{-1} and 511 cm^{-1}, respectively (Fig. 5.2).

The theoretical predicted wavenumbers of rhodizonic acid correlated well with experimental observed ones. Only in the case of the stretching and bending modes of C=O and OH are differences within 23 – 200 cm^{-1} observed as a result of the effect of hydrogen bonding. In addition, within 3550 – 3300 cm^{-1} are observed a series of bands typical for ν_{OH} of water molecules, included in the rhodizonic acid. Evidence of the well predicted IR-spectrum follow from elimination of the bands at 814 cm^{-1} and 565 cm^{-1} (Fig. 6.2).

4. Conclusions

By means of linear-polarized IR-spectroscopy of oriented solid samples as colloid suspensions in anematic liquid crystal the experimental IR-band assignment of croconic and rhodizonic acid in the solid-state were measured. Similar to squaric acid and its hydrogensquarate the $\nu^{s}_{C=O}$ is shifted to higher frequency than $\nu^{as}_{C=O}$. In the case of rhodizonic acid the typical tendency for opposite shift of these bands is observed. Experimental data are supported by theoretical calculations of the electronic structures and vibrational analysis of neutral acids at DFT level of approximation with the 6-311++G** basis set.

Acknowledgements

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